



# CHEMICAL ABSTRACTS

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## 1—APPARATUS

C. G. DERICK

The business of buying laboratory equipment. J. H. WILSON. *Can. Chem. Met.* 7, 39-40(1923). F. J. C.

A chromoscope for measuring the hydrogen-ion concentration of liquids by colored indicators. CH. O. GUILLAUMIN. *J. pharm. chim.* 26, 452-4(1922); cf. *C. A.* 16, 2344.—A sketch of the app., devised after the comparator of Hurwitz-Meyer and Ostenberg, is shown, and the description of its use is given. S. WALDBROTT

Simple method for the fractional distillation of small amounts of liquids. FRANZ LANYAR AND LUDWIG ZECHNER. *Monatsh.* 43, 405-412(1923).—Modifications of Emich's app. for detg. b. p. in a capillary tube (*C. A.* 12, 1433) are described which render possible the fractional distn. of 2-3 drops (0.05-0.2 g.) of a mixt. Essentially the same results are claimed as in the ordinary fractionation of large amts.

C. J. WEST

A new viscosimeter for very viscous substances. R. FISCHER. *Seife* 45, 483-4 (1922); *Chimie et industrie* 9, 89(1923).—A jacket in which water circulates at 62° surrounds a tube contg. the sample, the temp. of which remains const. at 58°. The time required for an Al ball to fall the length of the tube is noted with a stop watch. Pure glycerol is taken as standard, and the viscosity is expressed as the ratio of the time of fall with the sample to that with glycerol. With dark or opaque liquids the Al ball is made to close an elec. circuit and light a lamp. A. P.-C.

Elastic column dynamometer for hardness testing. H. A. HOLZ. *Chem. Met. Eng.* 28, 269-70(1923); illus. E. J. C.

Some notes on the evolution of the konimeter. R. A. H. FLUGGE-DE SMIDT. *J. Chem. Met. Mining Soc. S. Africa* 23, 77-86(1922). E. J. C.

New calculation for the determination of the strength of flanges. OSWALD KLINCK. *Chem. App.* 10, 3-4(1923).—Mathematical formulas. J. H. MOORE

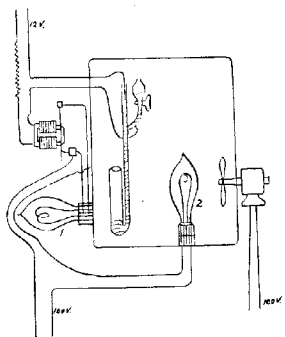
A net micrometer for use in making mold counts. B. J. HOWARD. *J. Assoc. Official Agr. Chem.* 6, 50-1(1922).—The use of a drop-in eyepiece micrometer ruled in squares equal to  $\frac{1}{4}$  of the diam. of the opening in the eyepiece diaphragm is suggested to help eliminate the personal factor in the analyst following the direction "no field should be counted positive unless the aggregate length of filaments present exceeds approx.  $\frac{1}{4}$  of the diam. of the field" in the Association's methods for tomato products. As the size of the opening varies in diff. makes of eyepieces the disk should be ruled after careful measurement. H. A. LEPPER

Accurate bubble meters for very small rates of gas flow. TYLER FUWA AND G. A. SHATTUCK. *Ind. Eng. Chem.* 15, 230-1(1923).—Curves show the effect of varying the diam. of the discharge tip, and the effect of the d. of the metering liquid on the vol. of gas delivered. The effect of surface tension was also studied by using soap solns. and found to have but a slight effect. D. E. SHARP

Modified form of double slit spectrophotometer. A. L. NARAYAN AND G. SUBRAHMANYAN. *Phil. Mag.* 43, 662-3(1922).—An electromagnetically maintained pendulum carrying a double slit is mounted in front of the collimeter slit of the spectro-

graph. This arrangement is free from the defects of Vierordt's type, and possesses many of the advantages of the sector photometer. D. C. BARDWELL.

**Air thermostat regulated electrically.** HAJIME ISOBE. *J. Chem. Soc. Japan* **43**, 650-3(1922); see fig.—I.'s thermostat has an extra lamp outside of the thermostat in the same circuit with the heating lamp. Thus



when the temp. becomes higher than a set point, and the contact between the wire and adjuster (Hg) is broken, the current flows through both lamps whereby the heat of the heating lamp became  $\frac{1}{2}$  instead of zero as in ordinary thermostats. When the temp. goes below the point, the current flows through only the heating lamp, (2) By this device, low heat capacity of the air is compensated and undercooling of the air is largely prevented. With an ordinary Hg-toluene adjuster (Ikeda), the temp. of this thermostat is maintained within  $\frac{1}{30}^{\circ}$ , and with a more sensitive adjuster, it is not difficult to maintain it within  $\frac{1}{100}^{\circ}$ . For an ordinary size thermostat 50 v. W or C lamp are satisfactory; for a const. temp. room, 2 microme wire resistance coils are so adjusted that 7 kw. are used for heating, and  $1\frac{1}{2}$  kw. are used while cooling.

**Another agitator.** D. H. KILLEFFER. *Ind. Eng. Chem.* **15**, 321(1923); cf. C. A. S. TASHIRO.

**A glass-metal joint.** M. I. DUNDON. *J. Am. Chem. Soc.* **45**, 716-7(1923).—A successful method of joining soft glass and Cu and Cu-plated steel tubing is described. E. J. C.

**An industrial protective mask.** H. A. GARDNER. *Paint Mfrs. Assoc. of U. S.*, *Circ.* No. 169, 132-3(Feb. 1923)—Description of a mask found satisfactory for use by spray painters, lead workers, etc. Illus. F. A. WERTZ

**Filter presses.** H. PLAUSON. *Can.* **228**, 443, Jan. 30, 1923. A hollow cylindrical filter is built up of superimposed elements, having irregular surfaces, the interstices being filled with a colloid; it also has a worm to discharge solid matter retained by the filter.

**Filter for milk of magnesia.** S. R. KING. U. S. 1,443,918, Jan. 30.

**Filter for air and gases.** H. KLUG. U. S. 1,443,134, Jan. 23. Filtering material is supported in successive layers helically arranged.

**Drying apparatus for recovering solvent vapors by condensation.** A. S. O'NEIL. U. S. 1,443,547, Jan. 30.

**Apparatus for analyzing flue gases.** R. F. MACMICHAEL. U. S. 1,443,492, Jan. 30. Flue gas and air are drawn by sep. suction fans through humidifying and temp.-controlling app. and the amt. of  $\text{CO}_2$  in the flue gas is indicated by a recording drift gauge depending on the differential pressures of the gas and air.

**Electric discharge tubes.** G. HOLST and E. OOSTERHUIS. *Can.* **227**, 894, Jan. 9, 1923. Rare gases in elec. discharge tubes are purified by introducing P into the tubes.

**"Telethermometer."** W. A. BAKER. U. S. 1,444,771, Feb. 13. Specifies a particular construction of elec. app.

**Funnel automatically actuated by electric current.** TOYO NEMOTO and TÔTARÔ ISHII. *Japan.* **40**, 101, Sept. 28, 1921. The funnel delivers a definite quantity of the

same liquid into bottles or other vessels. The delivery orifice is closed by an elec. device controlled by the pressure of the air current leaving the vessel.

**Drying apparatus.** TETSUJIRŌ YAMADA. Japan. 40,086, Sept. 28, 1921. Drying tubes are fixed horizontally in an oven and the sample is sent successively through the tubes.

**Ladle-drying apparatus.** G. R. McDERMOTT. Can. 228,316, Jan. 23, 1923. A liquid fuel burner extends through a cover and both are suspended over the ladle and means are provided for supplying compressed air and fuel to the burner.

**Reversing furnace mechanism.** M. C. STRESE. Can. 228,132, Jan. 16, 1923.

**Rotary horizontal furnace or kiln adapted for heating granular or pulverulent material.** A. DWORZAK. U. S. 1,443,529, Jan. 30. The kiln is surrounded by concentric chambers for hot gases and cooling water.

**Gas generator with washing apparatus.** ROBERT MÜLLER, KOMANDIT-GESELLSCHAFT. Ger. 346,325. The app. consists of a conical flask fitted with a stopper which contains the essential features of the device. This consists of a tube, furnished with a funnel at the upper end and terminating in a trap at the lower end, through which the liquid used in generating the gas is introduced. The gas after generation passes through a washing app. of annular cross-section fixed concentrically with the upper part of the tube. J. C. S.

**Gas-testing apparatus.** T. R. ERNEST. U. S. 1,442,868, Jan. 23. Gas, e. g., a gas electrolytically produced, which is to be tested for safety for storage is passed at atm. pressure through a receptacle in which a spark is produced at intervals, in order to test the gas for explosive qualities. If an explosion occurs the flow of gas is automatically cut off.

**Apparatus for testing abrasives.** I. RATNER and M. SCHWARZ. U. S. 1,444,803, Feb. 13.

**Scleroscope.** G. WIRNER and A. C. MOYER. U. S. 1,444,228, Feb. 6. The app. comprises a hammer moving in an open-ended tube with a cylinder and manually operated piston mounted on its upper end for actuating release mechanism for the hammer.

**Scleroscope.** R. HERRMANN. U. S. 1,444,606, Feb. 6. The device comprises a gravity-actuated hammer mounted with a driver device to return the hammer to its starting position. U. S. 1,444,607 relates to a similar app. adapted for testing the hardness of metals.

**Vapor box and column system for fractional distillation of petroleum, coal tar or other liquids.** F. M. HESS. U. S. 1,443,742-3, Jan. 30.

## 2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

**The best college course for the chemist.** R. F. ROSE. *Ind. Eng. Chem.* 15, 304-5 (1923). E. J. C.

**An experience with the general intelligence test in teaching freshmen chemistry.** JACOB CORNOG and EDWARD BARTOW. *Ind. Eng. Chem.* 15, 301-3 (1923). E. J. C.

**A national focus of science and research.** GEO. E. HALE. *Reprint & Circ. Series, Natl. Research Council*, No. 39, 515-30 (1923). E. J. C.

**The new Sterling chemical laboratory of Yale University.** B. B. BOLTWOOD. *Ind. Eng. Chem.* 15, 315-9 (1923). E. J. C.

**Traugott Sandmeyer's researches and discoveries.** HANS HAGENBACK. *Helvetica Chim. Acta*, 6, 134-86 (1923). E. J. C.

**Charles Frederick Mabery.** ALBERT W. SMITH. *Ind. Eng. Chem.* 15, 314 (1923).—A brief biography, with portrait. E. J. C.



Émilio Noeltling. A. HALLER. *Bull. soc. chim.* 33, 1-5. FRÉDÉRIC REVERDIN AND AMÉ PICTET. *Helvetica Chim. Acta* 6, 110-28(1923); *Bull. soc. chim. ind.* 1922-3 (Nov.-Dec.-Jan), p. 6-7.—Obituaries, with portrait and bibliography in the last 2 journals. E. J. C.

A Hungarian predecessor of Pasteur. JULIUS PREYSZ. *Chem.-Ztg.* 47, 111 (1923)—A very brief biography of Moritz Preysz. He discovered the process of pasteurization before the discovery by Pasteur, but because his publications were in the Hungarian language he has not been given credit. He also traced the cause of a "Pest" (nature not stated) in Budapest to impure well water, and as a result there was erected a water-works system in 1868. E. H.

Eirini-d'Eyrins, a forgotten predecessor of Pasteur. M. A. RAKUSIN. *Chem.-Ztg.* 46, 1069(1922). E. J. C.

The chemical work of Pasteur. GABRIEL BERTRAND. *Industrie chimique* 10, 3-10(1923); *Chimie et industrie* 9, 1-14(1923).—An address. A. P.-C.

Bibliography of scientific literature relating to helium. E. R. WEAVER. *Bur. Standards, Circ.* 81, 32 pp.(1923).—The literature from the time of the discovery of He to Jan. 1, 1922, is covered. E. H.

Twenty-ninth annual report of the committee on atomic weights. Determinations published during 1922. G. P. BAXTER. *J. Am. Chem. Soc.* 45, 563-72(1923); cf. *C. A.* 16, 1037.—The detns. reviewed are on H, O, Be, B, N, Na, Cl, Ga, Se, Br, Y, Ag, Sb, La, Tl, Pb, and Hg. Recent developments in isotopy are referred to. E. J. C.

A linear relation for certain atomic volumes. WILHELM BILTZ. *Z. anorg. allgem. Chem.* 117, 84-90(1921).—See *C. A.* 16, 3775. H. G.

New theories of valency. E. B. R. PRIDEAUX. *Chem. Age* (London) 8, 138-9 (1923).—A review. E. J. C.

Some views on chemical affinity. J. R. PARTINGTON. *Chem. Age* (London) 7, 850-2, 884-6(1922).—A summary of the modern thermodynamical treatment of chemical affinity. JAMES M. BELL

Classifying and measuring color by the Ostwald method. H. T. TENEN. *Am. Dyestuff Rep.* 12, 127-32(1923). E. J. C.

The ultimate structure of materials as a cause of their technically important properties. F. RINNE. *Glückauf* 58, 1505-7(1922).—An explanation of the differing behavior of fluid and solid materials with respect to viscosity, cleavage, brittleness, etc., due to their mol. arrangement and cryst. structure (cf. Rinne, *Das feinbauliches Wesen der Materie nach dem Vorbilde der Kristalle*, 2nd Ed., 1922). C. C. DAVIS

The significance of crystal structure. WM. H. BRAGG. *J. Chem. Soc.* 121, 2766-87(1922).—A lecture. It is demonstrated that whole mols. of org. compds. exist as such in the crystal lattice and that the symmetry of the crystallographic system, and hence that of the unit cells, are detd. by the symmetry of the mol. Thus a single asym. mol. in a cell gives triclinic symmetry, while higher symmetry is attained by grouping 2 or more asym. mols. about planes of symmetry, etc. The no. of mols. per unit cell is ascertained from X-ray data. Several examples of monoclinic and orthorhombic org. crystals are cited. G. L. CLARK

The structure of organic crystals. WM. H. BRAGG. *Proc. Roy. Inst. Gt. Britain*, 8 pp.(1922). (Separate.) Cf. *C. A.* 16, 2504, 3016, and preceding abstr. G. L. C.

The struture of benzene. M. L. HUGGINS. *J. Am. Chem. Soc.* 45, 264-78(1923); cf. *C. A.* 16, 3468.—Hull's interpretation of his X-ray data is satisfactory if the atoms are taken as *point scattering centers*, but, insofar as arrangement of layers over each other is concerned, must be discarded upon consideration of electronic arrangement. His data, with that of Debye and Scherrer, indicate for graphite a structure of closely packed benzene complexes similar to Körner's proposed *centroid* model. Assuming

such a structure in cryst.  $C_6H_6$  and its derivs., the dimensions of the benzene hexagon are computed for a dozen of these derivs. from crystallographic data, and in all cases the dimensions are within a few % of the corresponding magnitudes in graphite.

A. E. STEARN

Processes in the stretching of zinc crystals. I. General description of the phenomena and research methods. II. The quantitative consideration of the stretching mechanism. III. Relationships between the fiber structure and the tenacity. H. MARK, M. POLANVI AND E. SCHMID. *Z. Physik* 12, 58–72, 78–110, 111–6 (1923).—These papers present the results of extraordinarily extensive and detailed expts. The underlying phenomenon is as follows: If a metal wire is stretched beyond the limit of elastic deformation, an equil. point is reached where no further extension takes place in spite of the diminished cross section and representing a state of tenacity which has been produced by the stretching process. A *fibrous structure* is disclosed in the X-ray examn. in which there is a definite orientation of the single crystals and of the crystal planes within each crystal of metal with respect to the axis of wire (hence the direction of the stretching or drawing). The processes which go on during stretching are detd. in great detail for uni-cryst. wires of Zn. The detns. involve X-ray examn., optical observations, etch figures, etc. The following are the *criteria of the uni-cryst. nature of a wire*: the smooth bright cleavage planes; the absence of grain boundaries and parallel etch bands in metallographic cuts; definite goniometric and X-ray reflections during rotation; formation of parallel series by elliptical and oblique glide lines; the formation of flat bands by the stretching; the goniometric and X-ray identity and parallel position of planes in the ends of the pieces of a wire broken apart. The glide layers which are formed by the action of the stretching force suffer twistings which actually put a limit upon the stretching process. By means of these twistings an orientation of the lattice results, on account of which the glide planes, regardless of the initial positions, become definitely placed relative to the wire axis at a more or less acute angle ( $2^\circ$  to  $15^\circ$ ). This final angle is an inverse function of the temp. If this angle of the glide planes is known it is possible to predict the ductility from the orientation of the lattice in the original wire. In the two kinds of stretching, flat horizontal and secondary, different lattice planes serve as glide surfaces; in the first case the basal most closely packed planes and in the second, the prismatic surfaces of the first type (second most closely packed planes). Since the first type of stretching is very much greater it follows that the basal planes glide much more easily. Brittle crystals are those in which the basal planes lie practically parallel to the wire axis and hence do not permit of stretching. In the basal gliding the displacement is not in the direction of the greatest drawing force but in the direction of the digonal axes corresponding to the most closely packed edges of the hexagonal lattice which lie nearest the direction of the force. The existence of a known crystallographic glide direction has as a consequence that the final orientation which the lattice assumes in the stretching process will be absolutely detd. Flat stretching and twisted gliding are phenomena true also of *Sn, Bi, Al* and *Pb*. In every case by means of the bent gliding there is a re-orientation of the lattice so that the glide direction lies approx. parallel to the stretching direction. In Zn ductility disappears in this change of orientation and a very considerable tenacity remains. In the case of the *technically important metals, Fe, Cu, Al, W, Mg, Au*, etc., it must be said, however, that the stretching orientation is not an important factor of tenacity, and that the fiber structure has little to do with it.

G. I. CLARK

Statistical anisotropy in crystalline media and its röntgenographic determination.

K. WEISSENBERG. *Ann. Physik* 69, 409–35 (1922).—The anisotropy of naturally produced *fibrous structures*—plastically deformed metals, castings, electrolytic precipitates etc., is a statistical effect produced by a particular arrangement of the micro-

crystals in aggregates. All the statistical possibilities of arrangement are considered and classified in anisotropy classes. The determination of the class and the micro-crystal arrangement within the class by means of X-rays is theoretically outlined. It is concluded that the crystal units after drawing or rolling a metal have the same or a greater no. of elements of symmetry than micro-cryst. aggregates parallel to the symmetry element, and that the structure of the crystal unit cannot in general be known from the individual symmetry of the lattice, since in the former case are presented only the most closely packed planes or glide-planes and directions approx. parallel or perpendicular to the axes of the strain produced in the metal.

G. L. CLARK

**Double compounds and mixed crystals. Racemic and pseudo-racemic substances.** PHILIPPE LANDRIEU. *Bull. soc. chim.* 31, 1217-41 (1922).—A theory of the internal structure of these types of compds. The cryst. product formed by the union of 2 different mols. may be classified under 2 groups, double compds. and mixed crystals. In double compds. the points of the space lattice are considered to be occupied by the ions of the mols. These ions are distributed regularly and periodically throughout the lattice in a way such as to establish electrostatic equil. between the charges. This explains the fact that mols. unite in simple mol. proportions to form double compds. Furthermore, double compds., should form only from electrolytes. Hence the abundance of double compds. formed between inorg. mols. and their great rarity between org. mols. In mixed crystals the space lattice points are considered to be occupied by either mols. or ions which are isosteric, in the sense used by Langmuir. It is the possibility of an ion or mol. replacing in the lattice any other ion or mol. with which it is isosteric which explains the formation of mixed crystals. *Isosterism*, more or less complete, is the basis of isomorphism and "syncrystallization." Thus is explained: the intimate resemblance necessary between isomorphous substances; the small heat effect accompanying the formation of mixed crystals; and the frequent occurrence of mixed crystals between non-dissociable org. mols. The idea is developed that truly racemic compds. have the same type of structure as do double compds. Truly racemic compds. should form only from electrolytes. Pseudo-racemic compds. are considered to be similar in structure to mixed crystals, and may form from either dissociable or non-dissociable mols.

R. H. LOMBARD

**Occurrence, chemistry and uses of selenium and tellurium.** VICTOR LENHER. *Trans. Am. Inst. Mining Met. Eng.*, Paper 1198-N, 20 pp.—L. discusses the chem. principles utilized in the detection and detn. of Se and Te, and describes the analytical methods followed by producers of Se and Te in the U. S. Se is obtained in great part from Scandinavian pyrites cinders. Greek and Spanish pyrites cinders carry a small amt. The sole native source is anode-slime from refining Cu produced from sulfide ores. Te is practically always associated with Au; It is also found in small amts. in numerous Cu ores, and in some Pb ores. Te follows the precious metals into the blister Cu and is recovered from the anode-slime. Uses of Se and Te are discussed and production information is given.

E. G. R. ARDAGH

**Molecular dimensions, molecular structure and viscosity of the halogens and their hydrides.** HARRY SCHMIDT. *Z. Physik* 12, 24-7 (1922).—A continuation of *C. A.* 16, 1524. Calcs. of the "mean cross-section" of the mols. of H and of the halogens and their hydrides are made from viscosity data. By using the Bohr value for the radius of the H atom, it is indicated, from the agreement of the calcd. "mean cross-sections," that the configuration of the halogen mol. closely resembles two continuous spherical arms, while that of the H mol. differs considerably, the "cross-section" calcd. from the viscosity data being larger.

HENRY C. PARKER

**Measurements of the vapor pressure of pure argon.** FRITZ BORN. *Ann. Physik* 69, 473-504 (1922).—Previous measurements by Crommelin (*C. A.* 8, 1040, 2515)

have been criticized and doubt cast on the purity of the material. B., using great care in the purification by glowing Ca and a Ca arc, obtains argon with a consistently lower vapor pressure than the older results both for solid and liquid. The triple point is 83.93° abs. at a vapor pressure of 512.17 mm. The b. p. is 87.48° abs. The vapor pressures of liquid and solid are represented by the following equations,  $p$  being in atm.: liquid,  $\log p = [-339.3/T] + 1.75 \log T - 0.006737 T + 1.0698$ ; solid,  $\log p = [-366.87/T] + 1.75 \log T - 0.002829 T + 1.0698$ . The temp. range covered is 65° to 91° abs. A no. of calcs. of related thermodynamic quantities are included.

E. D. WILLIAMSON

**Density of atmospheric nitrogen.** A slight anomaly in the air of Madrid. M. PAVÁ AND E. MOLES. *Anales soc. españ. fis. quim.* **20**, 247-54(1922); cf. C. A. **16**, 2624.—The normal d. of  $N_2$  obtained from the air of Madrid is  $L = 1.25681$ . The d. of air in Madrid corresponds with a slightly higher proportion of  $O_2$  than that normal for other places. The anomaly is due to the presence of more than the normal amt. of  $O_3$  and gases of the argon group.

L. E. GILSON

**Vapor pressure of hydrogen and new determinations in the region of liquid hydrogen.** H. K. ONNES AND J. P. MARTÍNEZ. *Anales soc. españ. fis. quim.* **20**, 233-42 (1922).—The vapor pressures of liquid  $H_2$  at temps. near its normal b. p. were measured using a He thermometer. By interpolation the b. p. of  $H_2$  at 759.549 mm. is given as 20.49°.

L. E. GILSON

**The preparation of active hydrogen.** Y. VENKATARAMAIAH. *J. Am. Chem. Soc.* **45**, 261-4(1923); cf. C. A. **16**, 3245.—V. has developed 4 new methods of activation—(1) continuous burning of O in H, (2) surface combustion of H and O on Pt, (3) the high tension arc in H and (4) heating of H in arcs of various metals. The test of activation was the action of the H on S to form  $H_2S$ . In the case of the simple combustion of O in H, the reaction itself activates the H—probably owing to an ionization of the H by the electrons emitted by the reacting mols.

L. T. FAIRHALL

**The density of a mixture of oxygen, carbon monoxide and carbon dioxide. Relations between the volume percent and weight percent.** PAUL SCHREIBER. *Z. angew. Chem.* **35**, 701-2(1922).—Calcs. are made from the laws of dil. gases. The results are plotted in graphical form, convenient for fuel engineers.

H. C. PARKER

**Application of an optical manometer to the measurement of the viscosity of gases.** J. E. P. WAGSTAFF. *Phil. Mag.* **45**, 84-8(1923).—An app. is described in which a gas is allowed to flow through a calibrated glass capillary tube into a pressure chamber connected with a large auxiliary reservoir. The chamber is closed above by a glass plate clamped over an opening 1.97 cm. in diam. on which rests a second glass plate. The thin layer of air between the two must be maintained at atm. pressure and is illuminated by mono-chromatic light and viewed from above with a microscope capable of detecting the closing in of circular interference rings or fringes toward the center. The no. of rings per unit time is a measure of the pressure change and hence of the viscosity of the gas  $\eta$ . The rate of flow is detd. by:  $p_1 v_1 = \pi a^4 (p_2 - p_1)^2 / 16 \eta l$ , where  $l$  is the length of the capillary,  $a$  its radius,  $p_1$  and  $p_2$  are the pressures at its two ends, and  $v_1$  is the vol. of gas flowing per sec. at the pressure  $p_1$ . If  $T$  be the time for the pressure in the vessel to rise from  $p_1$  to  $p_2$  and  $p' = p_2 - p_1$ , the following relation is true:  $\log_e \{1 + [p'/(p_1 + p_2)]\} - \log_e \{1 - [p'/(p_2 - p_1)]\} = \pi a^4 T p_2 / 8 \eta l s$  where  $s$  is the combined vol. of reservoir and chamber and  $p_1$  corresponding to the disappearance of a given no. of fringes  $N$  for light of wave length  $\lambda$  can be calcd. from:  $p_1 = 256 E P^2 N \lambda / 90 R^4$ , where  $R$  is the radius of the plate of thickness  $l$  and Young's modulus  $E$ , when clamped at its edge. Several sets of observations are given from which the viscosity of air is detd. as 1.811 dynes/sq. cm./unit velocity gradient, which is in close agreement with detns. by other methods.

S. C. LIND

**A new method for the separation of gas mixtures by diffusion.** G. HERTZ. *Physik. Z.* 23, 433-4(1922).—The method consists in admitting the gas-mixt. through the side of a tube in which a vapor is flowing at the proper rate, and collecting the lighter constituent that diffuses against the stream of vapor. Theoretically this should give the lighter gas in a pure state. Spectroscopically pure He was obtained in this way from a 30% He 70% Ne mixt. C. C. VAN VOORHIS

**The method of H. Thoma for the photographic study of diffusion in transmitters, condensers, catalyzers, furnaces, gas producers, etc.** HENRY DIETERLEN. *Chaleur & industrie*, May 1922; *Rev. ind. minérale* No. 48, 356-8(1922).—An app. is devised for detg. the diffusion accompanying heat transmission, condensation, combustion, catalysis, etc. Observations are made in a vertical glass chamber of rectangular cross-section above which is a chamber contg. a fan for drawing air through the observation chamber. The velocity is measured by a diaphragm and calibrated tube connected between the fan and central chamber. Below the latter are suspended blotting paper strips immersed in  $\text{NH}_4\text{OH}$ . Various geometrical openings are cut in thick filter paper dipped in  $\text{HCl}$  or  $\text{H}_3\text{PO}_4$  and the air is passed through them. The  $\text{NH}_4\text{Cl}$  or  $(\text{NH}_4)_2\text{HPO}_4$  forms clouds which are easily photographed. By application of the equations of ordinary and thermal diffusion, these results can be interpreted qualitatively and quantitatively in their relation to hot and cold diffusion. Photographically lighter streams represent gas having given up its heat to a cold medium, and the dark streams those not deprived of heat by contact. C. C. DAVIS

**The properties of liquids in the state of saturation in the neighborhood of the critical point.** F. ARIÈS. *J. phys. radium* 3, 411-21(1922).—A. develops the relations obtaining between the limiting values of the various thermodynamic coeffs. in the neighborhood of the crit. point, as governed by the following assumptions: (1) "If  $\Delta P$  and  $\Delta T$  represent small finite variations in the immediate neighborhood of the crit. point, then  $\lim \Delta P / \Delta T = (\partial P / \partial T)_c = a$ , where  $a$  represents a quantity between zero and infinity. (2) The contact between the satn. curve and its tangent at the crit. point is of the first order." An equation for the variation of the heat of vaporization,  $L$ , as a function of the temp.  $T$  is given:  $L = (T_c - T) [\alpha \log (T_c - T) + \beta] + \gamma (T_c - T)^{1/2}$ .  $\alpha$ ,  $\beta$  and  $\gamma$  are const., detd. by 3 exptl. detns. This equation conforms to the relations required in the neighborhood of the crit. point as derived from A.'s assumptions. HENRY C. PARKER

**A critical review of Trouton's law, and its applicability at the triple-point.** SASI BHUSAN MALL. *Phil. Mag.* 45, 94-7(1923).—A crit. review of the Trouton const. from which it is concluded that there is no particular temp. at which Trouton's law holds, neither does it appear to have theoretical significance. The fact that the law holds approx. for a few selected substances when the vaporization is less than 1 atm. is regarded as accidental. S. C. LIND

**The shape of the capillary surface formed between a flat glass plate and a uniform circular cylinder, and the accurate determination of the surface tension of liquids.** J. E. P. WAGSTAFF. *Phil. Mag.* 45, 88-94(1923).—A very elegant method, from the theoretical and mathematical standpoint, for the detn. of surface tension of liquids. A rectangular glass plate about 2 cm. wide is clamped inside a glass cylinder about 5 cm. in diam., so that its two long edges are in accurate contact with the length of the glass cylinder. Upon dipping into a vessel contg. liquid, the latter is drawn up into the space between the plate and the cylinder. Upon viewing the meniscus along lines vertical to the plate its projection on the plate appears as a U-shaped curve. By making the plate the plane of the  $X$ - $Y$  axes and by taking the origin at the height corresponding to the stand of the liquid outside, the  $x$ - $y$  distances are detd. for various points along the curve by means of a traveling microscope capable of vertical and horizontal motion.

These values are introduced into the equation of the curve, the two members of which, plotted against each other, give a straight line with inclination  $\theta$  and  $\cot \theta = 2T/\rho g$ , in which  $T$  is the surface tension,  $\rho$  is the density of the liquid, and  $g$  is gravity. The surface tension of water at  $18^\circ$  was detd. as 74 dynes/cm. S. C. LIND

**Determination of capillary constants of various alcohols and their water mixtures.**

ELISA LAAMANEN *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 4, 7 pp. (1922).—By the method of rise in capillary tubes, the capillarity consts. (*i. e.*, twice the value of surface tension expressed in mg. per mm. divided by the d. of the liquid) at  $18^\circ$  of distd., tap, and sea water are 14.89, 14.70, and 14.03, resp. For MeOH and PrOH and their aq. solns. the following values were found:

%MeOH	100	90	80	70	60	50	40	30	20	10
const.	5.68	6.32	6.74	7.09	7.59	7.92	8.50	9.49	10.20	12.32
%PrOH	100	90	80	70	60	50	40	30	20	10
const.	6.06	6.70	6.11	6.00	5.90	5.80	5.67	5.58	5.85	7.26

For the latter there are max. and min. points at 90 and 20%, resp. The const. for AmOH is 6.02.

BENJAMIN S. NEUHAUSEN

**Determination of the specific gravities and volumes of mixtures of nitrobenzene, petroleum and toluene at various temperatures.** E. W. YLÖNEN. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 7, 18 pp. (1922).—The sp. gr. and vols. from 0 to  $100^\circ$ , of petroleum (P),  $C_6H_5NO_2$  (N) and  $C_7H_8$  (T) and of binary mixts. are given. By comparing the calcd. and observed ds. of mixts. of known vols. of the constituents, it is found that there is a contraction in case of N and P, a dilatation in case of P and T, while in mixts. of T and N there is a contraction for mixts. contg. more than 60% T and a dilatation when T is less. As temp. increases the degree of contraction is somewhat increased while dilatation decreases slightly. In the mixt. 9N + 1T there is a contraction at higher temps.

BENJAMIN S. NEUHAUSEN

**Precipitates formed in inorganic growths.** J. WINCKELMANN. *Mikrokosmos* 16, 41-5 (1922); cf. C. A. 15, 1449.—After a brief mention of colloidal and amorphous inorg. ppts. expts. are cited on the formation of membranes both on micro and macro scales as well as various Liesegang rings in glycerol gelatin. BENJAMIN S. NEUHAUSEN

**Some observations on emulsoids.** F. W. TIEBACKX. *Pharm. Weekblad.* 60, 76-7 (1923).—Contrary to the view held by de Jong, T. considers emulsoids less complex than suspensoids. Hemoglobin, dextrin and Congo red are probably individual mols. in soln. Emulsoids represent the more stable form of the substance. Dehydration of gelatin, arabic acid, albumin or agar by treatment with EtOH changes the substance into the labile or suspensoid form of greater complexity. Tannins and soaps, which are sol. in EtOH, present an exception. Numerous colloids are produced by similar condensation processes. Dialysis of  $FeCl_3$  soln., whereby hydrolysis and subsequent removal of HCl occur, results in successive aggregation of  $Fe(OH)_3$  mols. until the colloid flocculates out.

A. W. DOX

**An objective demonstration of the molecular movement.** A. EHRINGHAUS. *Naturwissenschaften* 11, 42-3; *Kolloid-Z.* 32, 19-22 (1923).—By replacing mastic emulsions by other preps., brighter lantern projections of the Brownian movement were obtained than those attainable by the method of Perrin (C. A. 4, 2767). Mastic with an  $n$  value of 1.54 was replaced by substances of higher  $n$ , such as heavy barytes crown glass, heavy flint glass, Zn blend, anatase, cuprite, rutile, cinnabar and Sb glance. These were dried and pulverized in an agate mortar, rubbed with distd.  $H_2O$  for 10-20 min., and filtered through blotting paper. The filtrate contained particles  $0.5-5 \mu$  in diam. Detailed directions and precautions are given for the app. and the arrangement of the microscopic projection.

C. C. DAVIS

**The iso-electric condition of gelatin.** S. O. RAWLING AND WALTER CLARK. J.

*Chem. Soc.* **121**, 2830-43(1922).—The gelatin used was prepd. by electrophoresis methods as described by Sheppard, Sweet and Benedict (cf. *C. A.* **16**, 3783). Viscosities were measured with a capillary viscosimeter of the Ubbelohde type, working under a const. head of pressure (cf. *C. A.* **15**, 7). The min. viscosity of gelatin sols occurred at a  $p_H = 4.7$  at  $35.4^\circ$  in the presence of either  $H_2SO_4$  or  $AcOH$ . The amt. of acid required to produce a min. viscosity in a given vol. of the sol was not independent of the concn. of gelatin, but appeared to be a straight-line function of it. The actual quantities of  $H_2SO_4$  and of  $AcOH$  required to give min. viscosity and the same  $p_H$  were approx. the same (cf. Pauli, *Colloid Chemistry of Proteins*, pp. 31, 41, 45). When a soln. of gelatin made isoelec. ( $p_H = 4.7$ ) either with  $H_2SO_4$  or with  $AcOH$ , was dild. to 2 or 3 times its vol., its  $p_H$  remained const. The fact that in some cases the isoelec. point as detd. by electrophoresis occurs at a  $p_H$  value above that at which the min. viscosity occurs may be due to the presence of degradation products of the protein.

H. M. McLAUGHLIN

**Colloidal chemistry from the standpoint of electrochemistry.** I. MICHAELIS. *Kolloid-Z.* **31**, 246-51(1922).—The analogy between colloid particles and ions is very close as evidenced by calcn., based on Stokes' law and on Brownian movement. A soln. of colloid particles with their charges, conducts and behaves like an electrolyte. The colloid particle derives its charge from a fixed layer of adsorbed ions, usually negative, about which is a mobile layer of positive ions as  $H^+$ . To carry the analogy further, an "acidoid" is defined as a colloidal particle which is charged negatively with respect to the soln. and has a layer of H ions about it, thus corresponding to an acid. A "basoid" is positive and has  $OH^-$  ions in the layer about it corresponding to a base. An "ampholytoid" may be positive or negative according to the  $H^+$  concn. of the soln. and corresponds to an amphoteric electrolyte. At a certain concn. of  $H^+$  the particle will be neutral, which is called the isoelec. point. Among acidoids are silicic acid, agar, cellulose, and the noble metals. No basoids are known.  $Al_2O_3$ , iron oxide, and gelatin are ampholytoids. A satisfactory measure of the strength of acidoids, corresponding to acid strength, has not been found, but a colloid which remains negative in a large concn. of H ion may be called strong. When the H-ion layer about a colloid is replaced by metal ions, the process is analogous to salt formation. The mass-action law has been applied with some success to some enzymes, treating the dissociation according to the above analogy to acids.

M. KNOBEL

**The heat of coagulation of ferric oxide hydrosol with sodium sulfate.** F. L. BROWNE. *J. Am. Chem. Soc.* **45**, 311-21(1923); cf. *C. A.* **16**, 517.—The heat of coagulation of  $Fe_2O_3$  hydrosols of widely varying purity with 0.2 *N*  $Na_2SO_4$  soln. has been investigated with sols prepd. by 3 dissimilar methods: (1) oxidation of neutral  $FeCl_2$  soln. with  $H_2O_2$  and dialysis, (2) peptization of pptd.  $Fe_2O_3$  in  $FeCl_3$  soln., (3) addn. of varying amt. of HCl to a sol of high purity made by the first method. The fact that the same values for the heat of coagulation at a given purity and concn. are obtained with sols prepd. by all 3 methods indicates that  $Fe_2O_3$  sols represent an equil. defined by the temp., pressure, concn., and purity. The change in dispersity of the  $Fe_2O_3$  during coagulation does not involve a measurable heat effect. The heat effects observed during coagulation of sols of low purity are due to (1) dila. of the  $FeCl_3$  and HCl in the sols, (2) mixing of these electrolytes with the  $Na_2SO_4$ , (3) changes in the adsorption equilibria.

F. L. BROWNE

**The constitution of ferric oxide hydrosol from measurements of the chloride- and hydrogen-ion activities.** F. L. BROWNE. *J. Am. Chem. Soc.* **45**, 297-311(1923).—With the calomel and H electrodes, resp., measurements of the  $Cl^-$  and  $H^+$  activities have been made in  $Fe_2O_3$  hydrosol prepd. by Neidle's method (*C. A.* **11**, 3142) over a wide range of purity and concn. A special technic for using the hydrogen electrode in the

presence of dil.  $\text{FeCl}_3$  is described. From these measurements the distribution of electrolytes ( $\text{HCl}$  and  $\text{FeCl}_3$ ) between the  $\text{Fe}_2\text{O}_3$  and the dispersion medium is deduced. Sols having a total Fe concn. of 0.5 g. equiv. per l. and a purity less than 14 contain  $\text{Fe}^{+++}$ ,  $\text{H}^+$ , and  $\text{Cl}^-$  in the dispersion medium, while sols of higher purity contain only  $\text{Cl}^-$  and the positively charged colloid particles. At lower concn. the  $\text{Fe}^{+++}$  and  $\text{H}^+$  disappear from the dispersion medium at somewhat lower purity. It is shown by the effect of dextrose on the f. p. of the sols that in spite of the hydrous character of  $\text{Fe}_2\text{O}_3$  practically all the water present in the sol acts as solvent for substances dissolved in it.

F. L. BROWNE

The evolution of the ferric hydroxide molecule in water. S. VEIL. *Compt. rend.* 176, 101-3(1923).—In dehydrating  $\text{Fe}(\text{OH})_3$  there is also a modification of the residual mol. with a consequent increase in the coeff. of magnetization of the oxide from 1 to 30. For the hydroxide heated in sealed tubes at temps. varying from  $120^\circ$  to  $210^\circ$ , the coeffs. of magnetization based on Fe content are the same as for the oxides. The magnetic properties of oxides and hydroxides depend on the previous history of the materials. Hydroxides pptd. in the cold from  $\text{FeCl}_3$  and calcined will give an oxide with coeff. of magnetization of 1; the hydroxide itself has a coeff. 9.8. But if hydroxide is almost completely dehydrated by heating at  $120^\circ$  in sealed tubes, its coeff. is 4.8, and that of its calcined oxide 4.6. If the hydroxide is redissolved in  $\text{HCl}$  and again heated in sealed tubes its coeff. is raised to 28.5 and that of the oxide obtained from it to 24.1.

BENJAMIN S. NEUHAUSEN

Displacement of adsorption—a contribution to the practical application of the adsorption theory. C. VAN DER HOEVEN. *Chem. Weekblad* 19, 555-7(1922).—The method of van Immerheiser (*Collegium*, 1918, 293) is criticized. It is not sufficient simply to ext. leather with water in order to det.  $\text{H}_2\text{SO}_4$ , as part of it is kept back by adsorption. H., therefore, exts. with an 8%  $\text{Na}_2\text{HPO}_4$  soln. which, by displacing the adsorbed  $\text{SO}_4$  ions, makes it possible to wash out the  $\text{H}_2\text{SO}_4$  contained in the leather.

R. BEUTNER

Starch iodide. L. BERZELLER. *Biochem. Z.* 133, 502-8(1922).—I is not adsorbed by starch from  $\text{CCl}_4$  or  $\text{C}_6\text{H}_6$  solns. and in alc. soln. adsorption is less than from  $\text{H}_2\text{O}$ . This is not attributable to a favoring action of KI present in the  $\text{H}_2\text{O}$  soln.. Equil. is obtained when I is adsorbed from alc. soln. This adsorption of I by starch is related to the colloidal state of the starch, since both cellulose and dextrin adsorb less than does starch. It is a true adsorption phenomenon.

F. S. HAMMETT

Determination of refractive indices of various concentrations of calcium nitrate solutions at various temperatures. GUSTAV AHLMAN AND GÖSTA ENROOS. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 14, 7 pp.(1922).—The ds. of 4.38, 8.67, 13.22, and 17.44%  $\text{Ca}(\text{NO}_3)_2$  solns. are detd. at  $2.5^\circ$  intervals from  $10^\circ$  to  $35^\circ$  and  $n_D$  at  $2.5^\circ$  intervals from  $15^\circ$  to  $35^\circ$ . The  $n_D$  increment per 1%  $\text{Ca}(\text{NO}_3)_2$  is 0.0018 to 0.00184 at  $15^\circ$  and 0.00177 to 0.00171 at  $35^\circ$ . The mean coeffs. of expansion of these solns. are also given.

BENJAMIN S. NEUHAUSEN

Determinations of refractive indices of ammonium nitrate and potassium nitrate solutions as well as several mixtures of these. A. HJ. SAVOLAHTI. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 15, 10 pp.(1922).— $n_D$  and d. of 5% and 10%  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  solns. as well as mixts. of these salts were detd. at  $2.5^\circ$  intervals from  $15^\circ$  to  $35^\circ$ . In the mixts. observed d. and  $n_D$  agree perfectly with the additive law of mixts.

BENJAMIN S. NEUHAUSEN

The determination of viscosities of sodium sulfate and potassium sulfate solutions. GRETA TIGERSTEDT. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 5, 8 pp.(1922).—The d., relative and abs. viscosities at  $10^\circ$ ,  $20^\circ$ ,  $30^\circ$ ,  $40^\circ$ , and  $50^\circ$  of 0.1, 0.2, 0.5, 0.8 and 1 N  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  and 1.5 N  $\text{Na}_2\text{SO}_4$  were detd. The relative viscosity of



$\text{Na}_2\text{SO}_4$  solns. increases more rapidly than the concn. while that of  $\text{K}_2\text{SO}_4$  is almost proportional to the concn.

BENJAMIN S. NEUHAUSEN

**Determination of viscosity of solutions of sodium and potassium tartrates.** TOINI KANTELE. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 6, 6 pp.(1922).—The relative and abs. viscosities and densities at 10°, 20°, 30°, 40°, and 50° of 4, 2, 1.5, 1, 0.5, 0.25 and 0.125 *N* Na tartrate and K tartrate have been detd.

BENJAMIN S. NEUHAUSEN

**The mode of reaction of highly insoluble or undissociated salts.** B. S. NEUHAUSEN. *Science* 57, 26(1923).—Reaction of  $\text{HgS}$  with I and pptn. of  $\text{HgS}$  from  $\text{KCN}$  solns. of  $\text{Hg}(\text{CN})_2$ , when max. time intervals for appearance of ions are considered, necessitate the conclusion that reactions at low concns. are between mols. or complex ions. (Cf. *C. A.* 16, 2459.)

BENJAMIN S. NEUHAUSEN

**The dissociation constants of sulfoacetic and  $\alpha$ -sulfofropionic acids.** H. J. BACKER. *Proc. Acad. Sci. Amsterdam* 25, 359-63(1922).— $\alpha$ -Sulfocarboxylic acids are dibasic. The free acids behave as strong acids and the acid salts as weak acids. The fact that the anilide of  $\alpha$ -sulfofropionic acid is a strong acid indicates that the stronger acid function belongs to the  $\text{SO}_3\text{H}$  and not to the  $\text{CO}_2\text{H}$  group. The 2nd dissoc. const. was detd. for each acid as follows: sulfoacetic,  $k_2 = 8.9 \times 10^{-6}$ ; sulfofropionic,  $k_2 = 6.0 \times 10^{-6}$ .

A. W. DOX

**The hydrolysis of platinum salts. II. Potassium bromoplatinate.** E. H. ARCHIBALD and W. A. GALE. *J. Chem. Soc.* 121, 2849-57(1922); cf. *C. A.* 15, 215.—Solns. of  $\text{K}_2\text{PtBr}_6$  whose concn. varied from 0.002 to 0.04 *N* ( $N = \text{K}_2\text{PtBr}_6/4$ ) were much more rapidly hydrolyzed under the influence of light than solns. of  $\text{K}_2\text{PtCl}_6$ . The rate of hydrolysis was measured by titration of the acidity with  $\text{Ba}(\text{OH})_2$  and with Congo red as an indicator. The acidity increased at first rapidly, then more slowly to a max. and finally decreased to an equil. that varied with the concn. of the soln. When solns. were prepd. and kept in the dark no change could be detected for 3 days. The acidity then rose slowly without showing a max. to an equil. corresponding with the final acidity reached in the light. A 0.02 *N* soln. which had reached equil. in light became neutral in 40 min. in the light after addition of enough  $\text{KBr}$  to give a 0.05 *N* soln. of  $\text{KBr}$ . This reversal of the reaction was also accelerated by light. H. M. McLAUGHLIN

**The anomaly of strong electrolytes especially with reference to the theories of J. C. Ghosh.** H. J. S. SAND. *Phil. Mag.* 45, 129-44(1923).—The present status of the Ghosh theory (*C. A.* 12, 1609, 2268; 13, 88) is critically reviewed. Boltzmann's theorem is applied to est. the degree of association of a completely ionized electrolyte in a medium of uniform dielec. const. Born and Lande's formula is used to est. the probability of an ion's obeying the inverse square law. Ghosh's virial formula is discussed. An equation is deduced thermodynamically for the heat of diln. of an electrolyte whose osmotic pressure obeys a law similar to those of Ghosh and of Milner, both of which are subjected to exptl. tests by means of data from various sources. It is concluded that the van't Hoff factor  $i$  is not solely dependent on the influences here considered, and it has not the same value for all equimol. solns. of electrolytes of similar type. In the exptl. cases reviewed the values of  $(n-1)$  from Ghosh's formula agree in order of magnitude with expt. The mean values for binary chlorides in aq. soln. of  $(2-i)$  as calcd. from Ghosh's formula gives better agreement than from Milner's.

S. C. LIND

**The curve of the change of the volume of water and the change which it undergoes by dissolving sodium chloride and urea.** M. C. DEKRUYZEN. *Nederland. Tijdschr. Geneeskunde* 66, I, 2304-13(1922).—Complicated empirical formulas and curves represent the change of the vol. of water with the temp., and the same for solns. of  $\text{NaCl}$  and solns. of urea.

R. BRUTNER

**Distillation of acetone-methanol; methyl acetate-methanol; and acetone-methyl acetate; and of 2-furaldehyde in water.** HILDING BERGSTRÖM. *Svensk Kem. Tids.* 34, 81-4(1922).—A mixt. contg. 90% acetone and 10% MeOH has a const. min. b. p. MeOH can be completely freed from acetone by distn., but the resulting acetone contains about 10% MeOH. The following figures represent % by wt. of AcOMe in soln. and in vapor, resp., of a mixt. of AcOMe and MeOH: 1, 3.1; 3, 9.2; 10, 26.4; 25, 48.0; 40, 60.4; 55, 69.2; 70, 75.7; 82, 82. The mixt. contg. 82% AcOMe b. 53.5°. Mixts. of acetone and MeOAc contg., resp., 17 and 62% acetone gave distillates in 3 fractions each varying not more than 1 or 2 % in compn. from the original mixt. The vapor from a 0.1% aq. soln. of 2-furaldehyde contains 0.7% furaldehyde. That from a 4.5% soln. contains 19.0%. The curve for the intermediate values is regular. A. R. ROSE

**Diffusion in solid solutions.** H. WEISS AND P. HENRY. *Compt. rend.* 175, 1402-5 (1922).—The velocity of diffusion of Ag into Au as measured by color zones of alloy doubled for a 50° temp. rise between 835° and 935°. Diffusion did not take place uniformly owing to the presence and orientation of metal crystals. The data are in accord with the law of diffusion in fluids as formulated by Tammann, though the accuracy is not felt to be sufficient to be a crit. test of this application of Tammann's equation.

A. E. STEARN

**The system sodium sulfate-sodium chromate-water. II.** YUKICHI OSAKA AND RYOEI YOSHIDA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 6, 49-54; *J. Chem. Soc. Japan* 43, No. 12(1922).—A continuation of the work of Takeuchi (cf. *C. A.* 10, 2174) using the same exptl. methods. The homogeneous equilibria of the system  $\text{Na}_2\text{SO}_4\text{-Na}_2\text{CrO}_4\text{-H}_2\text{O}$  at 28°, 31° and 33° are described and illustrated with diagrams. At 28° and 31°,  $\text{Na}_2\text{CrO}_4$  is tetrahydrated and its soly. as the decahydrate in  $\text{Na}_2\text{SO}_4$  decreases with increase in temp. The mol. fractions of  $\text{Na}_2\text{CrO}_4$  in the satd. solid solns. are 0.16 at 28° and 0.04 at 31°. This satd. solid soln. is not a compd., for the mol. fraction of  $\text{Na}_2\text{CrO}_4$  at 22° is approx. 0.8 (unpublished data of Takeuchi). C. C. DAVIS

**Determination of the heat of dilution of sodium carbonate solutions.** RAUHA LAKSONEN. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 12, 14 pp.—A water calorimeter was used, and the agreement ranged from 1 per mille to 3%. Several equations are given, e. g., if  $n = 15$  moles  $\text{H}_2\text{O}$ /s moles of salt,  $[Q_2^{15^\circ}]_{n^{100}} = (-106709 + 533.5n)/(n + 24.8)$ . This holds to 1 per mille for values of  $Q_2$  down to -428.

W. P. WHITE

**Determination of the heats of solution of the chlorides of sodium, potassium, ammonium, calcium, strontium and barium with the ice calorimeter.** LYYLI LEHTONEN. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 13, 9 pp.—Seven copics. were tried for each salt, from 0.0625 or 0.03125 to 4 or 2 N. The worst discrepancy, in an apparently typical series, is 6 per mille. Agreement is around 1% with Scholz (*Wied. Ann.* 44, 193(1892)) for KCl and NaCl, and to 3% or better with Winkelmann (*Pogg. Ann.* 149, 1(1873)) for  $\text{NH}_4\text{Cl}$ . For the anhyd. alk. earth chlorides, where previous detns. are limited, there was found for 0.0625, 0.25 1 and 2 N solns., resp.: CaCl<sub>2</sub>, 144.18, 142.63, 138.86, 135.29; SrCl<sub>2</sub>, 80.17, 78.87, 75.05, 71.11; BaCl<sub>2</sub>, 9.24, 8.45, . . . . ., 5.392.

W. P. WHITE

**Application of the method of continuous variation to ebullioscopic phenomena for determining double salts in solution.** F. BOURION AND E. ROUYER. *Compt. rend.* 175, 1406-8(1922); cf. Cornec and Urbain, *C. A.* 13, 1680, 1980.—A differential ebullioscopic method was used whose accuracy was of the order of that of cryoscopic methods. Maxima in compn.-temp. curves for mixts. of  $\text{CdCl}_2$  with the chlorides of K and  $\text{NH}_4$  show complexes of the form  $\text{K}_2\text{CdCl}_6$ . Iodide mixts. indicate analogous complexes.

A. E. STEARN

**Determination of the thermal expansion of copper- and zinc-sulfate solutions.**

HERMAN SUOMINEN. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 8, 6 pp.—Six strengths, from 0.1 to 2 *N* were investigated for each salt, at temps. from 0° to 60°, with a precision to within 1°. Both pycnometer and dilatometer were used for each detn. The expansion curves were not linear, and were noticeably less so for the more dil. solns. No discussion or formulas are given. W. P. WHITE

Notes on the electric heating of calorimeters. W. P. WHITE. *J. Wash. Acad. Sci.* 13, 17-28(1923).—The practical standard cal. to-day in the most accurate calorimetry is an elec. cal., and the outright adoption of this standard will tend to remove the very unnecessary confusion that now comes from having several different water-derived calcs., all less accurate. Detailed calcs. are given, showing how the running of an elec. calibration may be done with min. difficulty and error; and how the leads to the elec. heating coil may best be proportioned and arranged. W. P. WHITE

Personal equation errors in optical pyrometry. GEORG KEINATH. *Stahl u. Eisen* 43, 9-12(1923).—Comparable temp. measurements by unskilled operators using the total, and the partial radiation, and disappearing filament optical pyrometers from 600° to 1500° show the disappearing filament optical pyrometer to be most serviceable. Facilities in operation permit a rapid proficiency and an accuracy of  $\pm 20^\circ$  from 600-700°,  $\pm 15^\circ$  at 1000° and  $\pm 10^\circ$  at 1500°. Above 1500° the radiation pyrometer is used. W. A. MUDGE

Applications and limitations of thermocouples for measuring temperatures. I. B. SMITH. *J. Am. Inst. Elec. Eng.* 42, 171-4(1923). C. G. F.

The variation of the specific heat of air with temperature. J. R. PARTINGTON AND W. G. SHILLING. *Trans. Faraday Soc.*, advance proof, 1923.—A superior acoustic method with movable piston and elec. furnace was used, characterized by a triode oscillator, and a simple but effective listening device, which enabled maxima to be located to 0.1 mm., that is, usually better than to 1 per mille.  $C_p$  for air was found to be  $4.849 + 0.00036 T$  to 700°, and  $5.237$  at 800°, a little above the linear curve.

W. P. WHITE

Determination of the specific heats and specific weights of several minerals. ANNA DANNHOLM. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 9, 10 pp.—Marble, quartz, feldspar, a granite, scapolite, and soapstone were investigated for the sp. heats from 100° to room temp. The agreement was to 4% or better. W. P. W.

Determination of the specific heats of zinc and tin amalgams. J. MARTINEN AND J. R. TIHONEN. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 11, 10 pp.—Numerous data are given. The latent heat due to gradual melting makes the curves complex, and no general treatment of them was attempted. J. P. WHITE

Determination of the specific gravity and specific heat of antimony-lead alloys. J. A. LINNAVUORI. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 10, 13 pp.—Twenty-one different compns. were tested. The sp. gr. of the chilled samples was nearly always lower, sometimes 4%, than that calcd. by the mixt. rule; the sp. heats at temps. from 20° to 100°, detd. to about 1%, agreed with that rule. W. P. WHITE

Formation of acetylene and ammonia in incomplete combustion. K. A. HOFMANN AND ERICH WILL. *Ber.* 55B, 3228-33(1922).—When air is caused to form a flame in a combustible gas, the following amts. (in g.) of  $C_2H_2$  are formed per 100 g. of the combustible compd. decompd.:  $C_4H_6$  5,  $C_6H_5OH$  4.4,  $C_6H_5NH_2$  2.5,  $(C_6H_5)_2NH$  2.7, carbazole 2.4, pyridine 1.7, anthracene 1, quinone 1, and hexane 2. These results were obtained when the min. amt. of air was used to obtain a flame. From aniline, 3 g. of HCN are obtained and from carbazole, and diphenylamine 1.5 g. Various addn. agents in air forming a flame in H affect the yield of  $NH_3$ . The yield without any addn. agent was 3.1 mg. per 100 l.  $N_2$  in air. With 1%  $CrO_2Cl_2$  the yield is 0.0, with  $SiCl_4$  a trace,  $TiCl_4$  4.1,  $BCl_3$  4.3,  $OsO_4$  6.8, C dust 5.5,  $C_6H_6$  8.1.  $AsH_3$  added to the  $H_2$  gives no  $NH_3$ .

while  $C_6H_4$  added gives 4.3. Air burned in illuminating gas gives 8.0. With  $CHCl_3$  in the air 7.2;  $C_6H_6$ , 10.8, and with  $Ni(CO)_4$  in the illuminating gas, 16.5 mg. per 100 l. are obtained.

D. MACRAE

**Thermodynamics of the crystal lattice II.** M. BORN AND E. BRODY. *Z. Physik* 11, 327–52(1922); cf. *C. A.* 16, 1695.—The assertion made in the previous paper, that the Grüneisen law of the proportionality between at. heat and thermal expansion at low temps. is not valid, has been proved incorrect. Approximation formulas for the relation between temp. and the crystal const. are derived which rest upon the same principles introduced by Debye in the theory of sp. heat. Elasticity const., coeff. of expansion, and residual-ray wave length for the rock-crystal lattice type are calcd. under the assumption that the cohesion depends upon the electrostatic attraction of the ions and is proportional to a  $r^{-n}$  force. The value of  $n$  is calcd. from the densities and compressibilities of the crystals. From the agreement between the calcd. and observed elasticity const. it appears that the force acting between dissimilar ions is repulsive, and between similar ions, attractive, the latter force being about half as strong as the former over equal distance. The calcd. value for the residual ray wave lengths is also in good agreement with the observed. For the const.  $\gamma$ , introduced by Mie and Grüneisen, which relates the expansion coeffs. to the at. heat, two boundary values for low and high temps. are obtained. The values of  $\gamma$  found from measurements at ordinary temps. lie between these boundary values. It is therefore concluded that the assumption of a sp. monochromatic frequency is not sufficient for the calcn. of the thermal expansion.

E. N. BUNTING

**Dissociation equilibria by the method of partitions.** R. H. FOWLER. *Phil. Mag.* 45, 1–33(1923).—An extension (Part III) of the methods of Darwin and Fowler (*C. A.* 16, 4102; 17, 18) employing statistical mechanics to a theoretical and mathematical consideration of gaseous equil. The view, expressed in part II, is reiterated that the conception of entropy is not necessary in statistical work; an expression for entropy can be deduced statistically but not before all the relations which it would disclose are already known. In §2 the 2 previous papers are partly reviewed; in §§3–6 the simplest dissociation  $X_1 = 2X$  is considered. In §7 the results are applied to Saha's theory of thermal ionization (*C. A.* 15, 468, 3934) and it is concluded that a further term must be added to his ionization formula which may prove to be of great importance and which renders Saha's formula less definite. Detailed application of the new formula is postponed. In §8 a fundamental difficulty in the statistics of H (or of any other atom) is discussed. In §9 the results of §§3–6 are extended to the general dissociation problem. In §10 the general vapor pressure equation is tested. In §11 the general formulas for chem. const. are treated and it is shown that they depend on the lowest permitted quantum state of the mols. General consideration of the Nernst heat theorem and chem. const. derived from it are postponed to a later paper. S. C. LIND

**Partition functions for temperature radiation and the internal energy of a crystalline solid.** C. G. DARWIN AND R. H. FOWLER. *Proc. Cambridge Phil. Soc.* 21, 262–73(1922); cf. *C. A.* 16, 4102; 17, 18.—On the basis of certain assumptions regarding the ether and with the general principles of the quantum theory, a partition function is constructed from which are deduced Planck's law of temp. radiation and the Stefan-Boltzmann law of total radiation. The particular point in the demonstration is that these laws are obtained without any consideration of the mechanism of exchange of energy and without using the laws of thermodynamics except in so far as is necessary to define temp. From similar considerations, the partition function for any crystal is obtained which gives the usual formulas for the entropy, internal energy, and sp. heat of crystals. Additional remarks are given upon the construction of partition functions for systems obeying the laws of classical mechanics.

E. N. BUNTING

Rubbing the walls of a glass vessel with a glass rod. L. DEDE. *Z. Elektrochem.* 28, 543(1922); cf. *C. A.* 16, 3779.—A reply to Fricke (cf. *C. A.* 16, 3779). Reply. R. FRICKE. *Ibid.* 29, 44-6(1923). H. JERMAIN CREIGHTON

Electromotive behavior of aluminium. A. SMITS. *Z. Elektrochem.* 28, 543-5 (1922); cf. *C. A.* 16, 875.—Polemical against Günther-Schulze (cf. *C. A.* 16, 526, 1040). Reply. A. GÜNTHER-SCHULZE. *Ibid.* 545. H. JERMAIN CREIGHTON

Determination of electrical conductivity of solutions of zinc sulfate and copper sulfate and their mixtures. MARTTI AF HÄLLSTRÖM. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 20, 12 pp.(1922).—Cond. of 0.1, 0.25, 0.5 and 1 *N*  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  and mixts. of these salts were detd. at 5° intervals between 10-50°. On mixing equal vols. of the different salts in various concns., a cond. value somewhat larger than the mean of the 2 solns. is obtained. BENJAMIN S. NEUHAUSEN

The validity of Ohm's law for electrolytes under high field strengths. MAX WIEN. *Physik. Z.* 23, 399-403(1922).—After a series of expts. in which special precautions were taken to prevent any heating effect, the conclusion was reached that the variations from Ohm's law in electrolytes with applied field strengths up to 500,000 v. per cm. is less than 1%. C. C. VAN VOORHIS

Determination of electrical resistances of metallic powders and their mixtures with nonconducting powders. OSSIAN JÄÄMÄ AND YRJO E. G. LEINBERG. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 21, 20 pp.(1922).—The elec. resistance of finely powd. (going through 0.31-mm. mesh) Al, Zn, Ag, Cu, wrought Fe, brass, Sn, Sb, Ni, and cast Fe, mixed with varying percentages of marble, and of cast Fe with S, SiC, pumice and feldspar, and Sb with SiC and pumice were detd. at temps. of about 17.5-20°. As the proportion of admixed nonconductor increases, the resistance increases first gradually and after a point which is characteristic for each mixt. very rapidly. The resistance decreases appreciably with increase of pressure on the powder. BENJAMIN S. NEUHAUSEN

Determination of the dielectric constant and electrical conductivity of ice. HILMER BROMMELS. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 19, 5 pp. (1922).—By Nernst's method the dielec. const. of ice made by freezing  $\text{H}_2\text{O}$  in a condenser was found to have the following values for the temps. given:  $-2.1^\circ$ , 3.80;  $-5.9^\circ$ , 3.51;  $-10^\circ$ , 3.40;  $-14.2^\circ$ , 3.20;  $-17.6^\circ$ , 3.11. The elec. cond. ( $\times 10^{-9}$ ) of ice made in same way is as follows:  $-1.2^\circ$ , 0.388;  $-3.2^\circ$ , 0.398;  $-5.5^\circ$ , 0.409;  $-7.2^\circ$ , 0.417;  $-9.8^\circ$ , 0.432;  $-13.2^\circ$ , 0.450;  $-17.3^\circ$ , 0.473. Hence elec. cond. has a temp. coeff. of 1.2%. BENJAMIN S. NEUHAUSEN

Determination of the dielectric constants of toluene-petroleum and toluene-castor oil mixtures. PEKKA SIIVOLA. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 18, 7 pp.(1922).—The dielec. consts. (*D*) of toluene-petroleum and toluene-castor oil mixts. detd. according to Nernst's method are linear functions of the compn. For petroleum-toluene mixts. the following formulas hold:  $D$  at  $11^\circ = 2.684 - 0.00600 n$ ;  $D$  at  $21^\circ = 2.527 - 0.00489 n$ , in which *n* is % petroleum. For toluene-castor oil mixts.,  $D$  at  $12.5^\circ = 4.782 - 0.02144 n$ ;  $D$  at  $20^\circ = 4.554 - 0.02022 n$  in which *n* is % toluene. BENJAMIN S. NEUHAUSEN

The absorption of light in water solution of milk, (and suspensions of) lime and loam. TOIVO TUUKKANEN. *Soc. Sci. Fennica Commentationes Physico-Math.* 1, No. 17, 16 pp.(1922).—Beer's law describes accurately the absorption of light by various dilns. of milk with water. Suspensions of slaked lime and loam decrease in absorption with time owing to the suspensoids settling out. BENJAMIN S. NEUHAUSEN

The molecular scattering of light in *n*-pentane. RAMAVENKATASUBBA VENKATESWARAN. *J. Chem. Soc.* 121, 2655-63(1922).—The results show a satisfactory agreement with those calcd. from the Einstein-Smoluchowski formula. The degree of im-

perfection of polarization is small and shows a diminution near the crit. point, but does not change on passing through this point. W. ALBERT NOYES, JR.

**Explanation of some interference curves of uniaxial and biaxial crystals by superposition of elliptic pencils.** J. W. N. LÉHEUX. *Proc. Roy. Acad. Sci. Amsterdam* 24, 195-7; 25, 81-6(1922).—Mathematical.

E. J. C.

**The indices of refraction of phosphorescent sulfides.** MAURICE CURIE. *Compt. rend.* 175, 617-9(1922).—The  $n$ s were detd. by examg. them in S-Se mixts., the  $n$ s of which are 2.0 and 2.7, resp. In the various samples of sulfides of Ca, Ba, and Sr examd., it was found that the  $n$ s of different grains in the same sample were not the same, but the majority for all these substances had  $n$ s between 2.10 and 2.15. An appreciable fraction of the grains has a lower  $n$  (about 1.6) and is believed to be sulfate. The  $n$  of ZnS is much easier to det., and for  $\lambda = 630\mu$  is 2.35. By using these values and Lenard's and Schmidt's values of the dielec. const.,  $K$ , it is found that Lenard's interpretation concerning the constancy of the ratio  $\lambda/\sqrt{K}$  does not appear to be admissible.

E. P. WIGHTMAN

**Theories of the Kerr and Faraday effects.** K. F. HERZFELD. *Ann. Physik* 69, 369-84(1922).—The double refraction of transparent isotropic bodies under the influence of a strong magnetic field (Kerr effect) is considered from the quantum theory standpoint, (1) by a dispersion theory in which refractive indices and the position and strength of absorption bands are related; and (2) by a theory of the Stark effect for the relation of the position and strength of the absorption bands and the outer field. The different theories differ only in the latter point since they assume either a Stark effect of the usual kind upon the single mol., or different intensity change for different polarization directions by co-orientation of the mols., or an opposing effect of neighboring mols. Expts. indicate no advantage of one theory over the other. The Faraday effect (difference in refractive indices for right and left circularly polarized light which permeates in the direction of the magnetic lines of force) is similarly considered.

G. I. CLARK

**Polymorphism of antipyrine, vanillin and erythritol.** PAUL GAUBERT. *Compt. rend.* 175, 1414-7(1922).—Three modifications of antipyrine, 4 of vanillin and 2 of erythritol were prepd. using the proper precautions. These are described. A. E. S.

**Specific resistance of graphite.** W. ZEISS. *Z. Elektrochem.* 23, 527-8(1922).—Polemical against Rishkevich (cf. *C. A.* 16, 3424). Reply. E. RISHKEVICH. *Ibid* 528.

H. JERMAIN CREIGHTON

The theory of metallic conduction (BIALOJESKI) 3. The perchlorates of the alkali and alkaline earth metals and ammonium and their solubilities (WILLARD, SMITH) 6. Colloidal chemistry and electrochemistry (KOHLSCHÜTTER) 4.

### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

**The problems of atoms and radiation.** FRANZ SKAUPY. *Z. Physik* 12, 184-8(1922).—The interaction of the magnetic and electrostatic fields of electron orbits in different atoms has received too little attention. There is a possibility of getting away from the Bohr assumption of non-radiation electrons in their steady orbits. A simplification can be made in the assumptions necessary to give a qual. explanation of absorption, fluorescence, light emission from the atom and photoelectric action. A quant. study is needed for more exact and more extended applications. F. O. ANDEREGG

**The rotation of atomic axes in solids (with magnetic, thermal and chemical applications).** W. SCHOTTKY. *Physik. Z.* 23, 448-55(1922).—Three assumptions are

made: (1) the no. of quantum orbits is not greater for any arrangement of neighboring atoms than for the free atom; (2) by the absorption of a quantum of energy the axes of an atom may be turned  $180^\circ$  to another fairly stable position; (3) in solids at low temps. all the at. axes are turned in the same direction. Below the transition point of ferro-magnetic metals most of the atoms have their axes pointed in the same direction. A statistical equation is derived to apply to the properties of ferromagnetic and paramagnetic substances, especially at low temps. A similar equation is applied to at. and mol. heats giving results somewhat higher than the exptl. values of Lewis *et al.* (C. A. 13, 804) for Na, K, Mg and Ca, all paramagnetic. The significance of this viewpoint in understanding chem. consts. is pointed out. F. O. ANDEREGG

**The problem of two moving charges in its connection with the atomic theory.** S. BOGUSLAVSKI. *Phil. Mag.* 45, 145-60(1923).—The studies of Darwin (C. A. 7, 1327) and of Sommerfeld (C. A. 11, 232) of the orbits of electrons about a positive nucleus according to the Lorentz-Einstein formula for the variation of mass with velocity showed that in certain circumstances the electrons ought to describe spiral trajectories about the nucleus. The present treatment is still more general in assuming that the nucleus moves as well as the electrons. The conclusion reached is confirmatory of that of Darwin and of Sommerfeld that spiral trajectories in relative motion of the two charges are still obtained when the relative angular momentum is sufficiently small. S. C. L.

**The distribution of intensity of  $\alpha$ -rays in an absorbing medium.** R. M. SIEVERT. *Z. Physik* 12, 243-4(1922).—The so-called "isodoses" of Friedrich and Glasser (C. A. 17, 363) are liable to be in error by as much as 15%. F. O. ANDEREGG

**The passage of  $\alpha$  and  $\beta$  particles through gases.** DEBENDRA BOSE. *Z. Physik* 12, 207-17(1922).—Photographs made with an all-glass Wilson fog app., show the paths of H-rays generated by the passage of  $\alpha$ -rays through H gas, the long range of the H-rays, the fact that collision of  $\alpha$ -rays with H compds. does not produce H-rays, a few cases of great deflection of  $\alpha$ -rays, notable phenomena when  $\alpha$ -rays strike mica or glass surfaces, the ionization paths of  $\delta$ -rays produced by  $\alpha$ -rays passing through H, and the fact that branching of  $\beta$ -ray paths as well as their single and composite scattering are probable. F. O. ANDEREGG

**Significance of radioactivity in cosmic processes.** LISE MEYNER. *Z. angew. Chem.* 36, 9-11(1923).—A general discussion of the heat evolved by radioactive elements present on and below the earth's surface, and the age of the earth calcd. from radioactive relations. From the most reliable calcn. the age of the earth is 700 million years. The synthesis of heavier atoms from lighter ones (e. g., He from H atoms) with the evolution of energy to account for the loss in mass, is suggested as a possible source of energy such as is necessary to maintain the high temp. of the sun. D. C. BARDWELL

**The isotope conception, origin and development.** H. G. SÖDERBAUM. *Svensk Kem. Tids.* 34, 217-22(1923).—An historical discussion apropos the Nobel prize. Portraits of Aston and Soddy. A. R. ROSE

**The ionization and excitation potentials of nitrogen.** ERICH BRANDT. *Z. Physik* 8, 32-44(1921).—The difficulties in applying Bohr's theory (including the  $h\nu$  relation between ionization potentials and absorption lines) to di- and polyatomic mols. are discussed. The ionization potential of pure N was found to be 17.75 ( $\pm 0.1$ ) v. referred to the resonance potential of He at 20.5 v. Higher ionization steps were found at 25.41 ( $\pm 0.1$ ) v. and 30.72 ( $\pm 0.2$ ) v. A relation was found between an excitation potential at about 8.5 v. and the absorption band for N between 1870 Å. and 1250 Å. A detailed study of the resonance potential curve in this region showed a complex periodicity, which might account for band structure. D. C. BARDWELL

**The theory of metallic conduction.** TCH. BIAŁOBYJSKI. *Phil. Mag.* 45, 161-8(1923).—The free electron theory of metallic conduction has apparently met insuperable

difficulties in the "super-conductivity" of metals discovered by Onnes at about  $4^{\circ}\text{K.}$ , where the cond. becomes  $10^{11}$  times that at  $0^{\circ}\text{C.}$  B. adopts J. J. Thomson's theory of elec. doublets, but regards that portion of it involving intermol. field force as unsatisfactory, and proceeds to show that a quantum treatment of the theory gives a formulation which meets the difficulties imposed by super-conductivity. S. C. L.

**Emission of cathode and X-rays by celestial bodies.** HENRI DESLANDRES. *Nature* 110, 847-9(1922).—Recent developments in the study of ionization in the earth's atm. particularly at great altitudes, lend weight to the idea that X-rays and similar radiations play an important role in the phenomena observed in celestial spectra. The appearance of lines due to ionized Ca in the spectra of the sun and yellow stars can best be explained on the basis of a very penetrating radiation arising in the interior of the body. The solar corona and certain gaseous nebulas may owe their luminescence in part to the stimulation of these radiations, the existence of which is clearly proved in the case of the sun. K. BURNS

**Remarks on the work of E. Hjalmar concerning the M series of the elements.** A. DAUVILLIER AND LOUIS DE BROGLIE. *Compt. rend.* 175, 1198-1201(1922).—The recent spectrographic measurements of Hjalmar (*C. A.* 17, 680) are interpreted to confirm the theoretical predictions formulated on the subject of the structure of the Röntgen spectra of the elements (*C. A.* 17, 237; *Compt. rend.* 175, 755). It is assumed that the number of M and O levels and N levels are 6 and 10, resp. W. F. MEGGERS

**The evaluation of the colors of the spectrum in terms of the three primary colors.** R. A. HOUSTOUN AND ERIC DOW. *Phil. Mag.* 45, 169-76(1923).—A new and simple method is presented for the evaluation of the spectral colors in terms of the primary colors, employing the color triangle. A triangular diagram and set of values obtained by the method is given. In previous work insufficient attention has been given to the variation in performance of the same eye from day to day. S. C. L.

**Relative visibility of spectra when an electric discharge is passed through the vapors of alkali amalgams.** F. H. NEWMAN. *Phil. Mag.* 45, 181-9(1923).—The relative intensity of the spectra produced when an elec. discharge is passed through a mixt. of the vapors of Hg and the alkali metals is investigated. At  $100^{\circ}$  the Hg lines predominate, but at  $200^{\circ}$  the spectra of the alkali metals are brighter. The Na-D lines mask the Hg lines at the higher temp. The K spectrum is very faint under all conditions. An explanation of the effect is based on the low vapor pressure of the alkali metals at these temps., and on the low values of the ionization potentials which the vapors of Li, Na, K, Rb and Cs have. Employment of the amalgams of the alkali metals instead of the latter forms a useful and convenient method for obtaining the spectra of the alkali metals. The D-line radiation from Na amalgam is brilliant. S. C. L.

**The behavior of spectral lines at the positive pole of the metallic arc.** P. W. MERRILL. *Astrophys. J.* 56, 475-82(1922).—At the positive pole of the Pfund arc most Fe lines undergo an abrupt increase of intensity compared with that given by the core of the arc. In the region 3849 to 5763 Å. about 500 Fe lines were classified according to the amt. of this increase of intensity. The spark lines show the greatest increase and these lines may be found more readily by this means than by comparing spark and arc. The phenomena show a considerable degree of correlation with the temp. classification of furnace lines, those strengthened by high temps. being in general intensified at the positive electrode of the arc. The lines of Co and Ni show the same characteristics as those of Fe. K. BURNS

**Spectrum of active nitrogen as affected by admixture of the inert gases, with a note on the origin of the cyanogen band.** LORD RAYLEIGH. *Proc. Roy. Soc. (London)* 102A, 453-9(1922).—The after-glow observed when active N reverts to the ordinary type is due to a selection of the positive N bands. It is shown that this selection is



modified by large admixt. of the inert gases, the intensities in each group of bands being increased toward the red by the addn. He in particular intensifies the red group at the expense of the yellow and green groups. The initial effect of adding He, A, or Ne is the same, but an excess of A produces effects not obtained with He. No explanation of the phenomena is found. In the course of the expts. it was shown that a trace of C is necessary for the production of the cyanogen bands. K. BURNS

**The spark spectrum of gallium in air and in hydrogen.** ELLIAS KLEIN. *Astrophys. J.* 56, 373-9(1922).—The wave lengths of 83 lines were detd. in the region 2177 to 6414 Å. Of the 48 new lines found, none was a member of any known series. The use of H prevented the oxidation which takes place in air when the electrodes become heated, and H has few strong spark lines which might mask the metal spectrum. K. BURNS

**The carbon arc spectrum in the extreme ultra-violet.** F. SIMEON. *Proc. Roy. Soc. (London)* 102A, 484-96(1922).—By means of a vacuum arc and vacuum grating spectroscope the spectrum of the C arc was photographed from 600 Å. to 2512 Å., and the wave lengths of the prominent lines were redetd. Several lines new to the arc but prominent in the spectrum of the "hot spark" were found, and many lines were resolved into groups. Several of the latter had not previously been resolved. K. BURNS

**The secondary spectrum of hydrogen.** A. C. MENZIES. *Nature* 110, 876(1922).—Silberstein's particular soln. of the 3-body problem to explain the spectrum of neutral He was modified so as to apply to the negatively charged H atom and frequencies were then calcd. for integral values of  $n$  and  $m$ . (Cf. *C. A.* 17, 238.) As a result it was found that 47 lines in the secondary spectrum of H agreed with the calcd. values within an abs. error of 1 unit of frequency. Seven typical examples are given. W. F. MEGGERS

**The spectrum of neutral helium.** LUDWIK SILBERSTEIN. *Nature* 111, 46-7(1923).—Reply to Raman's criticism (*C. A.* 17, 684) of S.'s first paper (*C. A.* 17, 238). W. F. MEGGERS

**Spectrophoto-electrical sensitivity of some halide salts of thallium, lead, and silver.** W. W. COBLENTZ AND J. F. ECKFORD. *Bur. of Standards, Sci. Paper* 18, 489-98(1922).—The spectrophoto-elec. sensitivity of TlCl, TlBr, TlI, PbI<sub>2</sub>, AgCl, AgBr, and AgI were measured by exposing small samples of each to the energy emitted by a 600-watt W lamp (calibrated for equal energy) and by a quartz Hg arc lamp. Each sample was connected in series with a resistance, a potential of a few v. and a galvanometer. Galvanometer deflections were noted as the wave lengths of the energy falling on the salts were varied. The photo-elec. reaction of these salts is confined to a very narrow region in the violet. For the salts of Tl the max. of spectrophoto-elec. reaction is shifted toward the longer wave lengths with increasing at. wt. of the acid element in the salts. Of the halide salts of Pb only PbI<sub>2</sub> was found to react photo-electrically. For the Ag salts no definite relation was found between the max. of photo-elec. reaction and at. wt. of the acid element of the salt. C. C. KRESS

**The diffraction spectra produced by round particles irregularly distributed.** A. DRUVAULT. *Compt. rend.* 175, 1400-2(1922).—A qual. description of the diffraction phenomena produced on illuminating, with a narrow beam of white light, a glass plate on which a finely divided powder (lycopodium, spores of dry rot of wheat, desiccated blood) has been spread. The ordinary theory of diffraction does not account for the observed luminous effects which are to be explained by an inter-granular diffraction. C. C. KRESS

**The absorption spectra of thallium and indium vapor.** WALTER GROTRIAN. *Z. Physik* 12, 218-31(1922).—The known series arc spectra of the earth metals are portrayed graphically. They lead to the expectation that the auxiliary absorption series instead of the principle series will appear in the unexcited vapor of an earth metal. In Tl and In vapors the expected auxiliary absorption series was partly observed up to

high members. The difference in temp. with which the lines produced by passage from  $2p_1$  and  $2p_2$  to the same final orbit become observable must be as great as the term difference  $2p_1 - 2p_2$  and must increase in the earth metal group from Al to Tl. In Tl vapor this temp. is about  $400^\circ$  and in In,  $100-150^\circ$ . At high temp. in In vapor the absorption line  $\lambda = 2836.90$  was observed as in the emission spectra, but this line may not be included in the series scheme. In the earth metals the newly arriving electron is bound in an azimuthal 2-quantum orbit.

F. O. ANDEREGG

The monazite industry in its relation to rare earths and radioactivity (WHITE) 18. Bibliography on He (WRAVER) 2. Some microbiological consequences of the oxidizing properties of ThX (LEMAV, JALOUSTRE) 11C.

#### 4—ELECTROCHEMISTRY

COLIN G. FINK

**Electrochemical industries (in India).** L. L. FERMOR. *J. Indian Ind. Labour* 2, 444-6 (1922).—Numerous chemicals and metals appear to offer prospects of profitable electrochem. manuf. in India but elec. power rates will first have to be considerably reduced.

A. P. COUTURE

**Electric resistance furnaces.** C. R. DARLING. *Electrician* 90, 168 (1923).—Advantages of elec. heating vs. gas heating are enumerated. Ni-Cr alloys, in the shape of wire and ribbon, are widely used. They can be operated at  $1000^\circ$  for long periods of time without deterioration. For high speed steel treatment a resistor alloy that will operate at  $1300^\circ$  to  $1400^\circ$  is needed. D. believes that "a cheap alloy capable of withstanding  $1800^\circ$  without oxidizing" could be made.

C. G. F.

**Chromium electroplating.** ERIK LIEBREICH. *Z. Metallkunde* 14, 367-8 (1922); cf. C. A. 16, 377.—By the use of carefully reduced Cr salt solns. and lower c. m. f., adherent deposits of Cr on Fe, Cu, Ni and brass are obtained. L. showed (C. A. 16, 1656) that in the electrolysis of chromate solns. reduction took place in stages, that unexpected drops in potential took place and deposition of Cr was unsatisfactory. With carefully reduced Cr solns., however, and voltages from 2.2 to 3.6 and c. d. from 10 to 85 amp. per dm.<sup>2</sup>, Cr plated satisfactorily. A mat deposit could be made at the rate of 0.16 g. per amp. hr. (50% of theory). A bright deposit could be made only when half that rate was used. The mat plating can be made thicker and more dense by continued electrodeposition. A c. d. of 5 to 10 amp. per sq. dm., L. considers, in general, the best for Cr. Cr-plated metals resist corrosion by org. acids and by inorg. ones except HCl and hot H<sub>2</sub>SO<sub>4</sub>. Cr-plated cast Fe has stood up well in water for several months. The Reichsanstalt is testing Cr-coated metals and will publish results.

J. O. HANDY

**Notes on the electrolytic reduction of glucose.** ALEXANDER FINDLEY and V. H. WILLIAMS. *Trans. Faraday Soc.* 17, 453-6 (1922).—Analysis of electrolytic reduction products of glucose shows that no mannitol is obtained and only 40% of the theoretical amount of H is liberated. Formic acid and pentose are formed to a limited extent. Temp., kind of electrodes, and c. d. and concn. have little influence upon the electrolysis.

W. H. BOYNTON

**Colloidal chemistry and electrochemistry.** V. KOHLSCHÜTTER. *Kolloid-Z.* 31, 263-6 (1922).—The deposition of a metal on a cathode, though indicated by the scheme  $M^+ + \ominus \longrightarrow M$ , is really crystn. from a soln. Electrolytic ppts. are therefore dispersed structures. Crystn. nuclei and crystal growth vary with concn., temp., c. d., etc., so that electroplating and galvanoplastics have colloidal aspects. Each metal has characteristics, and the nature of the electrolyte is a factor. Colloidal compds. having

potent influence may be formed incidently or added intentionally. Unstable cryst. precursor forms may exist (explosive Sb), and morphologic changes affect the deposition potential. Colloidal adsorption films, otherwise unrecognizable, may cause overvoltage. At the anode there is a dispersion process indicated by the theoretical scheme  $M + \oplus \rightarrow M^+$ ; but passivity phenomena and polarization exceeding the normal potential show that the actual procedure is more complex. Metal ions passing into soln. may unite with anions (e. g., OH ions of water) and form nonconducting colloidal films, (e. g., hydroxides) which may adsorb gases or solutes. This film may be stripped off by a high frequency a. c. discharge, yielding an oxide sol.

JEROME ALEXANDER

**Technical electroösmosis.** P. H. PRAUSNITZ. *Kolloid-Z.* **31**, 319-23(1922).—Electroösmosis has been industrially used in the purification and partial dehydration of clays, peat, etc. Glue, gelatin, glycerol, nitrocellulose, beet sugar solns, serums and tanning solns. have been purified. The methods for clay purification are given in some detail. Clay in colloidal suspension may be pptd. in dense form by d. c. Emulsions may be broken down.

J. O. HANDY

**Electrical purification of industrial waste gases.** AUGUSTIN LAILLER. *Bull. soc. ind. Rouen* **47**, 573-94(1919).—A description of the principle of the Cottrell process and of application, especially of the elec. equipment required. A. P.-COUTURE

**Dielectric losses.** G. ALLSOP. *Beams* **12**, 105-7(1923).—A critical review of Höchstätter's equations. Six curves are shown. C. G. F.

**Maintenance of electric oscillations by a three-electrode tube.** F. VAN AALST. *Compt. rend.* **175**, 1397-9(1922).—The condition,  $R + (L - KM)/C\rho < 0$ , for sustained oscillations is experimentally verified. D. MACRAB

FAUSER, GIACOMO. **The Electrolysis of Water and the Synthesis of Ammonia.** Novaro, Italy. 52 pp.

Problem of durability of transformer oils (DELBIDGE) **22**. Manufacture of cyanamide (GARAIX) **18**. Colloidal chemistry from the standpoint of electrochemistry (MICHAELIS) **2**.

**Storage batteries.** H. LEITNER. U. S. 1,433,321-2, Jan. 23. Structural features. **Composition for electric battery boxes and similar articles.** L. M. COOPER. U. S. 1,444,587, Feb. 6. Battery or coil boxes or like articles are formed of a mixt. of leached wood ashes 1 pint, air-slaked lime 2 qts., linseed oil 0.5 pint, portland cement 0.5 pint and sawdust 0.5 bu.

**Electrolytic cell adapted for producing sponge lead and hydrogen sulfide from galena and dilute sulfuric acid.** W. E. GREENAWALT. U. S. 1,444,787, Feb. 13. The cell comprises horizontal electrodes of different polarities, one above the other, the upper electrodes being removable.

**Electrolytic diaphragm cell.** C. W. MARSH. U. S. 1,443,797, Jan. 30. A cathode is formed of 2 sections which, when joined, form an anode compartment. These sections and also the anode and diaphragm are mounted on a sectional surrounding body or shell, which serves as the cathode compartment.

**Battery connector.** H. E. FRASER. Can. 228,292, Jan. 23, 1923.

**Electrodes.** WM. G. MICHEL. Can. 228,442, Jan. 30, 1923. In making electrodes from powd. material the air is exhausted from the particles of material and a liquid binder is caused to occupy the voids thus created.

**Arc-lamp electrode.** H. B. EYNON. U. S. 1,444,961, Feb. 13. Negative arc-lamp electrodes are formed of a dense C shell with a core of less dense material such as C flour mixed with tar and  $C_6H_6$ , which is a good elec. conductor and a poor heat con-

ductor. U. S. 1,444,962 specifies negative electrodes formed with a C shell, a graphite core spaced from the inner wall of the shell and an intervening filling of powdered graphite mixed with a binder. Electrodes formed in this manner are adapted for use in projection app.

**Copper-nickel anodes.** S. GERTSEN. Can. 227,464, Dec. 26, 1922. Cu-Ni anodes contg. less than about 10% S are made by prolonging the blowing of Cu-Ni mat after practically all the Fe has been removed and maintaining the temp. sufficiently high by the addition of Fe, which is oxidized and slagged off. The anodes are used in the electrolytic refining of Ni.

**Electrolytic preparation of phenylhydrazine.** HIDEO WACHI. Japan. 40,194, Oct. 4, 1921. PhNHNH<sub>2</sub> is prepd. by electrolytically reducing Na diazobenzene-sulfonate in the presence of NaHSO<sub>3</sub>. The product needs no purification. The electrolyte is prepd. as follows: SO<sub>2</sub> is passed into a mixt. of PhNH<sub>2</sub> 25 g., Na<sub>2</sub>CO<sub>3</sub> 20 g., and H<sub>2</sub>O 300 g. until the soln. becomes clear and it is gradually dropped into the calcd. NaNO<sub>2</sub> neutralized with AcOH. Then 50 cc. of satd. NaHSO<sub>3</sub> soln. is added. Spongy Zn or Sn electrodes are used; the operation is conducted at 30-35°, with 7 v., and a c. d. of 5 amp. per sq. dm. Reduction is completed in 3 hrs. The product is isolated as hydrochloride by concentrating the soln. and adding HCl. For the *manuf. of antipyrine or pyramidone*, the soln. is used without isolation of the PhNHNH<sub>2</sub>.

**Pure iron by electrolysis.** A. SCHWIEDE. U. S. 1,444,887, Feb. 13. Fe is electrodeposited from a slightly acid soln. of FeCl<sub>2</sub> at a temp. of 85° or higher.

**Apparatus for electrical precipitation of suspended particles from gases.** E. ANDERSON and W. A. SCHMIDT. U. S. 1,444,092, Feb. 6. Gas is passed through a perforated collecting electrode toward a discharge electrode mounted opposite.

**Apparatus for electrical precipitation of suspended particles from gases.** E. ANDERSON. U. S. 1,444,997, Feb. 13.

**Apparatus for electrical precipitation of suspended particles from gases.** F. R. MCGEE and A. F. NESBIT. U. S. 1,444,845, Feb. 13.

**Production of zinc.** C. E. CORNELIUS. Can. 228,099, Jan. 16, 1923. The Zn ore is given a preliminary heat treatment to drive off moisture, before the extrn. step begins, in an elec. furnace in which the charge is agitated.

**Melting zinc in electric rotating furnaces.** C. E. CORNELIUS. Can. 228,098, Jan. 16, 1923. Zn powder is melted by continuously introducing it into a rotating furnace so as to subject the charge to a rubbing action to sep. the free liquefied content and continuously discharging the residue from the furnace.

**Electric furnace.** R. A. DRISCOLL. Can. 228,167, Jan. 23, 1923. An elec. furnace has a rotatably mounted inclined tube connected with an outlet in the furnace roof, means for rotating the tube, means for introducing charge materials into the upper end of the tube and auxiliary means for feeding material into the furnace.

**Electric furnaces.** F. W. SPERR and H. J. ROSE. Can. 227,463, Dec. 26, 1922. An elec. furnace for testing materials consists of a row of heating units forming a long narrow chamber to receive a testing tube and means for connecting the units in circuit progressively from one end to the other so as progressively to heat the sample of material being tested. The units are U-shaped, of refractory material wound with resistance wire.

**Electric resistance furnaces.** T. A. REID. U. S. 1,444,939-40, Feb. 13.

**Electric resistance furnace.** T. A. REID. U. S. 1,443,590, Jan. 30. Heating units within refractory walls include plates which are brought into operative position by a lateral and tilting movement.

**Electric resistance furnace.** G. M. LITTLE. U. S. 1,443,580, Jan. 30. The pat. relates to the manner of mounting and cooling the electrodes. The furnace is adapted for heating metals.

**Tubular resistance electric furnace.** G. M. LITTLE. U. S. 1,443,581, Jan. 30. A furnace adapted for baking green resistance rods is formed of tube sections (of graphite or other resistance material) held together end to end under pressure and surrounded by heat-retaining material, *e. g.*, lampblack and asbestos.

**Electric resistance crucible furnace.** C. H. CARPENTER. U. S. 1,444,948, Feb. 13.

**Tilting electric arc crucible furnace for smelting silver ore.** R. M. KEENEY. U. S. 1,443,024, Jan. 23.

**Tilting electric furnace adapted for melting scrap iron.** D. DeLUCA. U. S. 1,442,925, Jan. 23.

**Electric inductive furnace.** G. H. CLAMER and J. R. WYATT. U. S. 1,444,584, Feb. 6. The furnace has a resistor dome and is adapted for melting metals.

**Electric arc furnace.** F. A. J. FITZGERALD. U. S. 1,443,816, Jan. 20. The pat. relates to the manner of mounting opposed horizontal electrodes which are adjustable and extend through the side walls of the furnace. The furnace is adapted for use on single-phase current. Cf. C. A. 17, 371.

**Electric arc furnace of the rocking type.** W. E. MOORE, H. F. ALTER, E. A. HANFF, J. R. ECKLEY and F. WRIGHT. U. S. 1,444,980, Feb. 13. The furnace is adapted for melting steel.

**Rotating or oscillating electric furnace plants.** A. H. PRERSON. Can. 228,203, Jan. 23, 1923.

**Plating non-metallic surfaces with metal.** E. F. DIEYRICH. U. S. 1,444,113, Feb. 6. China, glass or other non-metallic surface to be coated with metal, *e. g.*, Ag or Au over Cu, is painted with a gelatin and graphite compn. or other glutinous and conductive material and the painted portion is then electroplated.

**Apparatus for electrolytic etching.** F. G. SCHWUCHOW and G. F. JOHNSTONE. U. S. 1,442,977, Jan. 23.

## 5—PHOTOGRAPHY

LOUIS DERR

**Effect of the addition of potassium ferrocyanide to a developer.** Research Lab. Eastman Kodak Co., *Report No. 1484*(1922).—With elon-hydroquinone, hydroquinone, and pyro developers and Eastman NC negative film,  $K_4Fe(CN)_6$ , up to 5%, did not affect density, contrast, shadow detail, or fog. L. DERR

**Theory of the development of the latent image.** M. VOLMER. *Phot. Korr.* **58**, 226-8(1921).—It is possible that the action of light on the Ag halide grain is merely an alteration of the packing of individual Ag atoms in the crystal lattice, and that the reduction of AgBr, normally slow, is greatly accelerated when catalyzed by the minute alterations in the grains affected by the light. L. DERR

**The silver germ theory of development.** S. E. SHEPPARD. *Phot. Korr.* **59**, 76-8 (1922).—Volmer's theories (cf. preceding abstr.) are criticized on the ground of preliminary formation of adsorption halide-developer complexes. Chromic acid desensitizes all emulsions. The sensitivity of fine-grained emulsions, but not of coarse-grained ones, may be restored or even increased in some cases. L. DERR

**Mercurous nitrate and sulfate as proportional reducers.** A. STEIGMANN. *Phot. Ind.* **1921**, 697.—A 0.5%  $HgNO_3$  soln. is used; if too rapid it is retarded by diln. or  $Hg_2SO_4$ . L. DERR

**Effect of temperature upon time of development of duplitized X-ray film.** Research Lab. Eastman Kodak Co., *Report No. 1315*(1922).—With 5 min. at 65° as a standard time for development, a 5° fall in temp. increased the time 30% and a 5° rise decreased it 23%. L. DERR

**Color prints by the new Badische Anilin u. Soda Fabrik process with diamine bases. Photometric behavior of such films.** J. M. EDER. *Phot. Korr.* 59, 89-91 (1922).—Many brilliant colors, except pure whites, may be obtained. Quinoline yellow has about  $\frac{1}{6}$  of the sensitiveness of AgCl paper to daylight. A table is given of the relative color sensitiveness of AgCl, quinoline yellow, and eosine benzidine papers. L. DERR

**Color photography.** J. G. CAPSTAFF and N. B. GREEN. U. S. 1,444,329, Feb. 6. The color ratio of a diapositive, consisting of a transparent base with different color records in register upon opposite faces, is corrected by submitting one only of the faces to the action of a soln. (such as alc. contg. 1% of  $\text{NH}_3$ ) which will lessen its color intensity.

**Three-color photography.** S. M. DE PROCOUDINE-GORSKY. U. S. 1,443,012, Jan. 23. See Brit. 168,100 (C. A. 16, 210).

## 6—INORGANIC CHEMISTRY

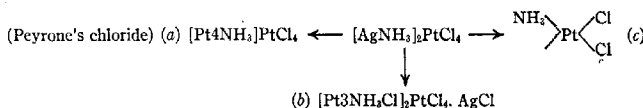
H. I. SCHLESINGER

**Reaction between silver perchlorate and iodine. Chlorine tetra-oxide.** M. GOMBERG. *J. Am. Chem. Soc.* 45, 398-421 (1923).—The action of I and Br on dry  $\text{AgClO}_4$  in anhydrous solvents was studied to find if  $(\text{ClO}_4)_2$  could be prepd.  $\text{Et}_2\text{O}$  proved the most suitable solvent. Purification of materials and exptl. procedure are described. A small amt. of a very labile I compd. was always formed and evidence was obtained for  $(\text{ClO}_4)_2 + \text{I} \rightleftharpoons (\text{IO}_4) + \text{Cl}$ . On the basis of this (quant.) evidence, exptl. methods were devised by which about  $\frac{2}{3}$  of this substance could be eliminated, leaving in the  $\text{Et}_2\text{O}$  pure  $(\text{ClO}_4)_2$ . Concns. above 0.1 N are not advisable.  $(\text{ClO}_4)_2$  is colorless, not volatile with vapor of  $\text{Et}_2\text{O}$  and is probably dimolecular in that solvent as is also  $\text{AgClO}_4$ . It is readily hydrolyzed, ultimately to  $\text{HClO}_4$  only, but evidence was found for  $2(\text{ClO}_4)_2 + \text{H}_2\text{O} = \text{HClO}_4 + \text{HOCIO}_4$ . It reacts with dry  $\text{Ag}_2\text{O}$ , liberates I from iodides but not in equiv. amts., reacts quant. with Zn and Mg to form perchlorates; with Fe, Sn and Cu to form salts of the metals in both valencies; slowly and incompletely with Cd, Bi and Ag.  $\text{Et}_2\text{O}$  solns. of pure anhydrous  $\text{HClO}_4$  and of  $\text{EtClO}_4$  were prepd. and responded differently to the tests characteristic of the tetra-oxide. A. R. M.

**The perchlorates of the alkali and alkaline earth metals and ammonium. Their solubility in water and other solvents.** H. H. WILLARD and G. F. SMITH. *J. Am. Chem. Soc.* 45, 286-97 (1923).—The perchlorates of Li, Na, K, Rb, Cs,  $\text{NH}_4$ , Ba, Sr, Ca and Mg, were prepd. pure and anhyd. and where hydrates existed these were also studied. Tables are given showing the solubilities at 25° of the anhyd. salts and of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  in water,  $\text{Et}_2\text{O}$ ,  $\text{EtOAc}$ , acetone, Me, Et, Pr, Bu and isobutyl alcs., and giving the phys. consts. of the solvents.  $\text{LiClO}_4$  is extremely sol., in anhyd.  $\text{Et}_2\text{O}$  but  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  and the other anhyd. perchlorates are practically insol. The purification and dehydration of the solvents are discussed. A. R. M.

**Complex platinum compounds. III. Molecular rearrangements observed with complex platinum compounds.** L. A. CHUGAEV and N. K. PSHENICYN. *J. Russ. Phys. Chem. Soc.* 52, 47-62 (1920); cf. C. A. 10, 3040.—The depolymerization of bi-complex salts of the type  $[\text{Pt}4\text{A}]\text{PtX}_4$  (where A = a mol. of  $\text{NH}_3$ , amine, org. sulfide etc.), resulting in the formation of the monomeric type  $[\text{Pt}2\text{A.X}_2]$  and in the accompanying transference of  $\frac{1}{2}$  of the total A mols. from one Pt atom to another, is frequently encountered among complex Pt compds., but has not previously been observed with the simplest purely inorg., in particular with the ammino-, complexes of Pt. This gap has now been filled by the authors, who show that tetraamminoplatinous platinochloride (Magnus's green salt) is capable of undergoing depolymerization in accordance

with the scheme  $[\text{Pt}4\text{NH}_3]\text{PtCl}_4 = [\text{Pt}2\text{NH}_3, \text{Cl}_2]$ , the chloride of Reiset's Base II being thus formed. The reaction is effected by cautious heating over a naked flame to  $270^\circ$ , and never proceeds to completion, part of the green salt decomposing with sepn. of metallic Pt. Expts. have been made also with certain heterometallic bicomplex compds. in which the Pt occurs only in the anion,  $[\text{PtX}]_n$ , while the cation is formed of another metal in combination with a known no. of  $\Delta$  mols. giving the so-called neutral part of the complex: e. g.  $[M, n\Delta]\text{PtX}_4$ . If as the component  $M$  is taken an element, such as Ag, Zn, Cu, Hg, etc., which, according to all the available data, holds mols. of  $\text{NH}_3$ , etc., less stably than does Pt, the transference of these mols. from the metal  $M$  to the Pt should take place with great readiness. With the aminiosilver platinichlorides, the transference of  $\text{NH}_3$  from the Ag to the Pt atom occurs at comparatively low temps.: At  $60\text{--}70^\circ$ , monoamminiosilver platinichloride yields, together with  $\text{AgCl}$ , also (a) tetraamminoplatinous platinichloride (Magnus's green salt), (b) chlorotriamminoplatinous platinichloride (Cleve's salt), and (c) *cis*-dichlorodiamminoplatinum



while at a higher temp. ( $100^\circ$ ) the last two compds. disappear and are replaced by (d) *trans*-dichlorodiamminoplatinum (chloride of Reiset's Base II); in either case, the loss of  $\text{NH}_3$  is negligible. At all temps. between  $100^\circ$  and  $200^\circ$ , diamminiosilver platinichloride yields a new product, namely, (e) tetraamminoplatinous chloride (chloride of Reiset's Base I), the loss of free  $\text{NH}_3$  being considerable. At  $100^\circ$ , the only compd., besides  $\text{AgCl}$ , accompanying  $e$  is  $a$ ; at  $150^\circ$ ,  $d$  also appears, while at  $200^\circ$   $a$  disappears and the  $d$  and  $e$  form the sole products. The chloride  $d$  is evidently a secondary product formed from  $a$ . When heated at  $50\text{--}60^\circ$ , diethylamminiosilver platinichloride readily undergoes transformation into the analogs of  $e$  and  $a$ , part of the ethylamine being liberated:  $[\text{Ag}2\text{NH}_2\text{Et}]_2\text{PtCl}_4 = 2\text{AgCl} + [\text{Pt}4\text{NH}_2\text{Et}]\text{Cl}_2$  and  $2[\text{Ag}2\text{NH}_2\text{Et}]\text{PtCl}_4 = 4\text{AgCl} + [\text{Pt}4\text{NH}_2\text{Et}]\text{PtCl}_4 + 4\text{NH}_2\text{Et}$ . Under the same conditions, monoethylamminiosilver platinichloride gives the analogs of  $a$  and  $c$ , part of the original compd. also decomposing with complete loss of the amine and formation of silver platinichloride. Tetramminozinc platinichloride,  $[\text{Zn}4\text{NH}_3]\text{PtCl}_4$ , gives, at  $111^\circ$ ,  $c$ ,  $a$ , and  $e$ . J. C. S.

Variation of the electrical conductivity among the ammoniacal derivatives of platinum nitrite. I. A. CHUGAEV AND N. A. VLADIMIROV. *J. Russ Phys. Chem. Soc.* 52, 135-8 (1920).—The values of  $\Lambda_{1000}$  for tetraamminoplatinous nitrite  $[\text{Pt}4\text{NH}_3](\text{NO}_2)_2$ , nitrotri-amminoplatinous nitrite  $[\text{NO}_2\text{Pt}3\text{NH}_3]\text{NO}_2$ , *cis*- and *trans*-dinitrodiamminoplatinum  $[(\text{NO}_2)_2\text{Pt}(\text{NH}_3)_2]$  and K platinonitrite are found to be, resp., 276.5, 96.5, 0.95, 2.42, and 302.4. The observed value of  $\Lambda_{2000}$  for nitrotri-amminoplatinous platinonitrite,  $[\text{NO}_2\text{Pt}3\text{NH}_3]\text{Pt}(\text{NO}_2)_4$ , is 217, the value calcd. by summation of the mobilities of the corresponding ions being 197.2 (cf. Chugaev and Kiltinovich, C. A. 11, 561). J. C. S.

Action of ammonium nitrate and of aqueous ammonia on copper. Properties of cupric-tetrammine nitrite and nitrate. HENRY BASSETT AND R. G. DURRANT. *J. Chem. Soc.* 121, 2630-40 (1922).—The corrosion of Cu and Cu alloys by  $\text{NH}_4\text{NO}_3$  in ammuniton results in the formation  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$  and small amts. of nitrite. Dry  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$  melts at about  $210^\circ$ , bubbles rapidly for a while and then explodes vigorously at about  $212^\circ$  leaving a residue of black  $\text{CuO}$ . At  $120^\circ$  in a vacuum the tendency of the dry tetrammine to lose  $\text{NH}_3$  is negligible. In moist air at the ordinary temp. the salt is slowly hydrolyzed with formation of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ . When Cu was left in 2*N* and 8*N*  $\text{NH}_4\text{OH}$  solns. in the absence of nitrate,

but exposed to the air, considerable quantities of nitrite were formed. For each mol. of  $N_2O_4$ , 25 and 23.9 mols of  $CuO$  were formed. When corrosion is rapid, about half the  $Cu$  in soln. is in the form of  $Cu(NH_3)_4(NO_3)_2$  and half as  $Cu(NH_3)_2CO_3$ .  $Cu(NH_3)_4(NO_3)_2$  was prepd. by 5 different methods and the above formula (rather than  $Cu(NO_3)_2 \cdot 2NH_3 \cdot 2H_2O$  proposed by Peligot) confirmed by analysis.  $Cu(NH_3)_4(NO_3)_2$  is exceedingly sol. in  $H_2O$ . When pure it may be heated rapidly or slowly without any explosion; but specimens contg. nitrate are apt to explode towards the end of the heating process. It loses more than 15% of the  $NH_3$  at temps. below  $100^\circ$ .  $Cu(NH_3)_2(NO_3)_2$  was obtained as a purple powder by heating finely powdered blue tetrammine nitrite for 24 hrs. at  $97^\circ$  in a tube provided with a loose glass stopper.  $Cu(NO_2)_2 \cdot 3Cu(OH)_2$  is prepd. by adding alc. to an aq. soln. contg. equiv. amts. of  $CuSO_4$  and  $KNO_3$ . After filtering from the heavy ppt., the dark green lac soln. is evapd. in the water bath and the basic nitrite seps. as a bluish cryst. deposit. When compared by the falling-wt. method of Robertson, the following figures give *sensitiveness to shock* on the basis of picric acid as 100:  $Cu(NO_2)_2 \cdot 3Cu(OH)_2$ , quite insensitive;  $Cu(NO_2)_2 \cdot 3Cu(OH)_2$  nearly so;  $Cu(NH_3)_4(NO_3)_2$ , 89;  $Cu(NH_3)_2(NO_3)_2$ , 89; 11%  $Cu(NH_3)_4(NO_3)_2$  and 89%  $Cu(NH_3)_2(NO_3)_2$ , 55;  $Cu(NH_3)_2CO_3$  > 120. The greater sensitiveness of the mixed tetrammine nitrate and nitrite is possibly connected with the higher  $O$  content of the former in conjunction with the readier loss of  $NH_3$  by the latter. D. MACRAE

**Decomposition and formation of calcium cyanamide.** V. EHRLICH. *Z. Elektrochem.* **28**, 529-42 (1922).—The decompn. of  $CaCN_2$  above  $1100^\circ$  is not detd. wholly by the temp. Above  $1200^\circ$  and more especially above  $1300^\circ$   $CaCN_2$  sublimes. At the latter temp. a small amt. of  $CaC_2$  is reformed from the  $C$  and  $CaCO_3$  contained in the  $CaCN_2$ . The  $CO$  produced in this reaction causes decompn. of the sublimed  $CaCN_2$  in the following ways:  $CaCN_2 + CO = CaO + 2C + N_2$ , and  $2CaCN_2 + CO = CaC_2 + CaO + C + 2N_2$ . Pure  $CaCN_2$  sublimes at  $1300^\circ$  without melting. Addn. of about 10%  $CaO$  reduces its m. p. to  $1200^\circ$ , while the addn. of 15%  $CaO$  lowers the m. p. to  $850-900^\circ$ .  $CaCN_2$  which is free from  $CO$  decomposes above  $1000^\circ$  in accordance with the equation  $(A) CaCN_2 \rightleftharpoons CaC + N_2$ . Addns. of substances to  $CaCN_2$  have no influence on the decompn. pressure at temps. below  $1200^\circ$ ; but above this temp. the decompn. pressure is reduced, owing to reduction in concn. due to sublimation of  $CaCN_2$ . Within the same range of temp. the pressure of  $N$  developed during the decompn. of  $CO$ -free  $CaCN_2$  is markedly less than in the decompn. of "lime-nitrogen." The presence of free  $C$  increases the decompn. pressure, probably owing to the influence of the reaction,  $(B) CaC_2 \rightleftharpoons CaC + C$ , which proceeds from right to left below  $1100^\circ$  and *vice versa* above this temp. The "lime-nitrogen" reaction in the form,  $CaC_2 + N_2 = CaCN_2 + C$ , expresses the net result of equations  $A$  and  $B$ . A primary formation of cyanide is improbable. Calcn. of the heat of formation of  $CaCN_2$  according to equation  $A$ , on the basis of the *Nernst* heat theorem, gives the value of 61400 cal. The heat of reaction of the "lime-nitrogen" reaction is probably higher than this. H. J. C.

**Monoclinic double selenates of the manganese group.** A. E. H. TUTTON. *Proc. Roy. Soc. (London)* **101A**, 225-45 (1922).—The prepn. of perfect crystals of the 3 obtainable salts in the system  $R_2M(SeO_4)_2 \cdot 6H_2O$ , where  $M$  is  $Mn$  and  $R = Rb, Cs$  and  $NH_4$ , is described. All attempts to prep. the  $K$  salt failed as was the case in the hexahydrated double sulfates. The morphologic and optical properties of the salts were detd. very completely. The same progression was found in all the properties with the progressive increase of at. no. of the alkali metal which had been observed in all the series previously investigated. The  $Rb$  and  $NH_4$  salts are almost exactly isostructural. A. R. M.

**Monoclinic double selenates of the cadmium group.** A. E. H. TUTTON. *Proc. Roy. Soc. (London)* **101A**, 245-64 (1922).—As in the  $Mn$  group only the  $Rb, Cs$  and



$\text{NH}_4$  salts could be prepd. as hexahydrates, the K salt apparently being incapable of existence. These salts present extreme difficulties of prepn.; the Rb and Cs salts were probably never before prepd. and the  $\text{NH}_4$  salt has not been optically investigated. The salts tend to be, or soon become, opaque and porcelain-like, rendering optical investigation impossible. Results, so far as they could be obtained, are in line with those obtained in other groups. A summary of this very complete study of the monoclinic alkali sulfates and selenates and the monoclinic hexahydrated double sulfates of the alkali metals and Mg, Zn, Fe, Ni, Co, Cu, Mn and Cd is appended and a bibliography of the 26 published papers of results and 5 papers describing new app. devised in the course of it. Begun in 1890 and now completed the work has included a study of 75 salts and complete measurement of over 800 crystals. The complete accord of the results with modern theories of atomic structure and with the results of X-ray analysis is pointed out.

A. R. MIDDLETON

**Preparation of sulfuryl chloride.** LEONCÉ BERT. *Bull. soc. chim.* 31, 1264-70 (1922).—For the prepn. of large amts. of  $\text{SO}_2\text{Cl}_2$  the method of Ruff (*Ber.* 34, 3509 (1901)) is most practicable but it contains two sources of difficulty. Cork stoppers, even protected by  $\text{Na}_2\text{SiO}_3$ , are soon disintegrated by hot vapors of  $\text{SO}_2\text{HCl}$  and  $\text{SO}_2\text{Cl}_2$  and the interior tube of a glass reflux is frequently fractured and entrance of water into the boiling  $\text{SO}_2\text{HCl}$  causes violent and dangerous explosions. These difficulties were overcome by covering the stoppers with several layers of asbestos paper cemented with  $\text{Na}_2\text{SiO}_3$  (Vorlaender and Schilling, *Ann.* 310, 372(1900)) and by using for the inner tube of the reflux an iron tube of 1 cm. interior diam., 1 m. length and 2 mm. wall-thickness, carefully scoured throughout the interior and so much of the exterior as projects into the flask. The iron is attacked but little and salts of Fe have practically no influence on the reaction. With a shorter tube the  $\text{SO}_2\text{Cl}_2$  contains considerable  $\text{SO}_2\text{HCl}$  and mercurous salt. A condenser jacket 70 cm. long is placed as close as possible to the upper end of the iron tube. The flask, of vol. 250 cc. for each 300 g. of  $\text{SO}_2\text{HCl}$  heated, is fixed in an inclined position. The condenser for  $\text{SO}_2\text{Cl}_2$  is set vertically and connected to the top of the iron tube by a glass tube of 8 mm. exterior diam., as short as possible, by means of asbestos thread impregnated with  $\text{Na}_2\text{SiO}_3$  at the iron and a Vorlaender stopper at the condenser. Provided a rapid current of cold water was maintained in this condenser, various types proved equally efficient and cooling the receiver by ice was unnecessary. After the entire app. has been carefully dried, the reflux jacket is filled with cold water and the tap closed; the  $\text{SO}_2\text{HCl}$  is brought to rapid boiling and as soon as vapor of  $\text{SO}_2\text{Cl}_2$  begins to appear in the second condenser, a very small stream of water is admitted to the first so as to maintain a temp. of 70-95°. Use of 1% of  $\text{HgSO}_4$  instead of 0.66% Hg gave yields 4% greater; 56% in 2 hrs.; 80% in 6 hrs. For greatest efficiency and economy, after heating 1 hr. substitute a fresh flask of  $\text{SO}_2\text{HCl}$ ; let the first cool;  $\text{HgSO}_4$  seps. almost completely and is filtered off by glass wool and used again; recover  $\text{SO}_2\text{HCl}$  by distn. and use the residual acid to generate HCl. After rectification by a 60-cm. Vigreux column the yield is 1500 g. of pure  $\text{SO}_2\text{Cl}_2$  for each 1200 g. of  $\text{SO}_2\text{HCl}$ . For prepn. of  $\text{SO}_2\text{HCl}$  use com. oleum of 70%  $\text{SO}_3$ , not over 1100 g. in a 1-l. flask, and displace air by HCl throughout the train before admitting the oleum. Connect to the flask a 50-cm. condenser, glass or iron interior tube, by a glass tube of at least 8 mm. diam., bevelled at both ends and having a lateral opening near the bevel in the flask. Satn. with HCl is evidenced by exit of this gas at the end of the train. Then replace the inlet tube for HCl by a tube carrying a thermometer and distil. An ordinary cork stopper easily endures distn. of 1 kg. of  $\text{SO}_2\text{HCl}$  and the product is colorless. Two kg. can be prepd. in 8 hrs. with a single app.

A. R. MIDDLETON

**Behavior of the stannic acids towards solutions of alkali hydroxides.** G. E. COLLINS AND J. K. WOOD. *J. Chem. Soc.* 121, 2760-65(1922); cf. *C. A.* 16, 1712,

3274.—The hypothesis that  $\beta$ -stannic acid is a salt-like complex formed by continued condensation between mols. of  $\text{Sn}(\text{OH})_4$  acting as acid and base, resp., and that accordingly the more complex varieties should be resolved by strong acids and bases into less condensed forms, is further examd. with reference to the behavior toward alkalis of different modifications of stannic acid. Both peptization and the reversal of the  $\alpha$ - $\beta$  change are brought about more easily by alkali hydroxides than by HCl on account of the preponderating acid properties of  $\text{Sn}(\text{OH})_4$ . With 0.8–1.1 *N* alkali part of the  $\beta$ -stannic acid was undispersed while the  $\alpha$ -acid was completely dispersed by KOH of this concn. but not by NaOH. That this was due to the greater ease with which the  $\beta$ -sols undergo coagulation, ionization of the salt formed by adsorption of alkali being repressed by excess of KOH in soln., was shown by removing the apparently insol. matter from the flasks contg. the  $\beta$ -mixts. and adding it to pure water when it readily dispersed. The critical concn. of KOH above which coagulation of  $\beta$ -sols takes place is 0.78 *N* as compared with 1.5 *N* for HCl. Ultra-filtration through collodion membranes showed that the concn. of KOH is much reduced by the process, which indicates that much alkali is adsorbed by the colloidal stannic acid and removed with it in ultra-filtration. A larger proportion of the total tin present passed into the ultra-filtrate than was the case with HCl, indicating a higher degree of dispersion by alkali than by acid of the same concn. The marked difference in the behavior of KOH and NaOH is explainable by the smaller soly. of Na stannate (Zocher, C. A. 15, 1468). In consequence of this a smaller concn. of NaOH than of KOH would cause coagulation of sols produced by peptization of  $\text{Sn}(\text{OH})_4$  by the two hydroxides, resp. A. R. M.

Some new series of phosphotungstates. F. KEHRMANN AND R. MELLE. *Helvetica Chim. Acta* 5, 942–4 (1922).—Three new series of salts are noted briefly. Slight acidification with AcOH of a very concd. soln. of Na phosphate and tungstate gives after some days a mixt. of 2 complex products; a microcryst. powder, little sol. in cold, easily in hot, water, but not recrystallizing from its solns. Prolonged washing with cold water gives products corresponding to  $14\text{MO}.5\text{P}_2\text{O}_5.19\text{WO}_3 + \text{aq.}$  or  $29\text{MO}.10\text{P}_2\text{O}_5.39\text{WO}_3 + \text{aq.}$  The other salt, very sol. in cold water, forms supersatd. solns. from which it may crystallize only after months. Analysis indicated  $3\text{MO}.4\text{P}_2\text{O}_5.6\text{WO}_3 + \text{aq.}$  The prepn. of Scheibler's salt (*Ber.* 5, 801 (1872)),  $5\text{NaOH}.3\text{H}_2\text{O}.2\text{P}_2\text{O}_5.6\text{WO}_3.13\text{H}_2\text{O}$ , was repeated and found to correspond to the ratio  $\text{P}_2\text{O}_5:7\text{WO}_3$ . It was identical with a salt previously described by K. (*Z. anorg. allgem. Chem.* 1, 437 (1892)), to which the formula  $3\text{MO}.2\text{P}_2\text{O}_5.7\text{WO}_3 + \text{aq.}$  was provisionally assigned. A. R. MIDDLETON

Tetrachlorodipyridinoiridates. Configurations of two series of tetrachlorodipyridinoiridites. MARCEL DELÉPINE. *Compt. rend.* 175, 1211–3 (1922); cf. C. A. 16, 535; 17, 898.—Oxidation of the dipyridinoiridites by  $\text{Cl}_2$ ,  $\text{HNO}_3$ , etc., yields the tetrachloroiridates ( $\text{IrPy}_2\text{Cl}_4$ ), nonelectrolytes, in two isomeric forms according as they are derived from the orange or the red iridite; Br water oxidizes the red but not the orange salt. The product from the orange iridite is pure black; that from the red, violet-black. Both are insol. in water. The former is here shown to be the 1, 2- and the latter the 1, 6- isomer. The *cis*-compd. is strongly dichroic and oxidizes both iodides and bromides according to  $\text{IrPy}_2\text{Cl}_4 + \text{MI} = \text{IrPy}_2\text{Cl}_4\text{M} + \text{I}$ ; the *trans*-compd. is not dichroic and oxidizes iodides but not bromides. Both decompose  $\text{NH}_3$  with formation of N; the *cis*-compd. is reduced to the orange  $\text{NH}_3$  iridite, the *trans*-compd. yields aminopyridino bases by a complicated reaction. The remarkable dichroism of the tetrachloro compd. from the orange iridite permitted detn. of its configuration very simply. Under definite conditions it can be syn-crystd. with  $[\text{PtPy}_2\text{Cl}_4]$ , proved by Werner to be the *cis*-compd. The crystals of the Pt complex acquire the dichroism of the Ir complex, which could result only in case of identical configuration. Hence the orange iridite is the *cis*- and the red iridite the *trans*- salt. A. R. M.

*cis*- and *trans*-Dichlorodioxalatoiridites. Optical resolution of the *cis*-potassium salt. MARCEL DELÉPINE. *Compt. rend.* **175**, 1408-11(1922).—The method of Vèzes and Duffour (*C. A.* **3**, 2912) should according to probability yield a mixt. of *cis*- and *trans*-isomers in the ratio 4:1; presumably they described the *cis*-salt. Heating to 100°, or better to 130° for 10 min., yields 60% of *cis*-salt, 12-15% of *trans*-salt, the balance being extremely sol. amorphous  $K_2Ir_2Cl_4(C_2O_4)_6$  ( $= 3K_2IrCl_5(C_2O_4)_3 - 2KCl$ ). Either isomer could be changed into the other by heating to 130°. The *trans*-salt forms large red crystals both monoclinic needles and triclinic prisms, both with  $4H_2O$ ; temp. of transition is above 40°. Also a pentahydrated monoclinic form seps. near 0°. The salt is dehydrated below 100°. Solns. of the two isomers react differently to salts of Ag and Tl. By strychnine salts the *cis*-isomer was resolved; the dextro form is the more sol. The rotatory power is small,  $[\alpha]_D = \pm 23.8^\circ$ , but very permanent, a soln. of the *l*-salt remaining unchanged 3 yrs.; it disappears after long heating at 130°. The active salts are more sol. than the *dl* form larger crystals, have  $3H_2O$  which they lose easily at 100°; the *dl* form has 1  $H_2O$  which it retains at 100°. A. R. M.

Reducing action of arsenious acid. MORITZ KOHN. *Monatsh.* **43**, 367-71(1923); cf. *C. A.* **16**, 536.— $AgNO_3$  in the presence of  $NH_3$  is completely reduced by excess  $As_2O_3$  to metallic Ag, with the simultaneous formation of  $H_3AsO_4$ . This reduction is not prevented by the presence of neutral salts, such as  $NaNO_3$  or  $Na_2SO_4$  but there is apparently a decrease in the  $HO$ -ion concn., since the velocity of the reaction is considerably decreased. The reduction of  $CuSO_4$  by  $As_2O_3$  in the presence of  $NH_3$  is likewise not prevented by neutral salts ( $KCl$ ,  $NaNO_3$ ). C. J. WEST

Preparation of hydrocyanic acid in large quantities in the laboratory. E. FRITZ-MANN. *J. Russ. Phys. Chem. Soc.* **52**, 227-34(1920).—For prep. HCN from  $K_4Fe(CN)_6$ ,  $H_2SO_4$  and  $H_2O$ , less of the last two ingredients than is usually recommended may be employed, the yield of the acid and the velocity of the reaction remaining unimpaired if the 3 reagents are taken in the proportions 10:5:8. The app. used is described.

J. C. S.

Borates. The system  $(NH_4)_2O-B_2O_3-H_2O$ . Temperature-concentration diagram. U. SBOGI AND L. FERRI. *Mem. accad. Lincei* [v] **13**, 570-91(1922).—The results previously obtained (*C. A.* **7**, 1685, 2001; **10**, 2586; **16**, 3597) are collected. J. C. S.

Some physical properties of sulfuric anhydride. H. S. *Industrie chimique* **10**, 11-3(1923).—A review on the  $\alpha$  and  $\beta$  forms. A. P.-C.

Working up iodine residues. F. ARNDT. *Chem.-Ztg.* **47**, 16-7(1923).—The reactions concerned in the method (*C. A.* **13**, 3101) are first  $2HI + 2HNO_3 = I_2 + 2NO + 2H_2O$  and then alternately  $2NO + O_2 = 2NO_2$  and  $NO_2 + 2HI = I_2 + NO + H_2O$ . For large amts. of residues (100-500 g. I in 10-20 l. solu.) the method is economical. The first I sublimed contains all the  $H_2O$ . It is dried and resublimed. The rest is pure after sublimation. Ferrous salts interfere by forming a brown addn. compd. with  $NO$ . This may be avoided by heating. If  $Hg$  is present in excess, the insol.  $HgI_2$  must be decomposed with  $HCl$  and  $KClO_4$ . The resulting I and Cl compds. are distd. into thiosulfate or sulfite soln. which is worked up in the usual way. Org. I compds. are treated the same way. If  $Hg$  is present with an excess of iodides, A.'s method may be used but there is a residuc of  $HgI_2$  which must be worked up afterwards. Pb salts are dissolved in crude fuming  $HNO_3$  and the soln. is decanted off the I which is then sublimed. If org. compds. whose volatility is similar to that of I are present, the I should be extd. with thiosulfate or sulfite soln. before treatment. Other org. compds. do not interfere.

W. STERICKER

Application of the method of continuous variation to ebullioscopic phenomena for determining double salts in solution (BOURION, ROUYER) **2**.

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

**Molybdo-manganimetry and its applications.** G. FONTÈS AND L. THIVOLLE. *Bull. soc. chim. biol.* **4**, 614-22(1922); cf. *C. A.* **15**, 3855; **16**, 1788.—Bertrand's method for sugar can be modified by dissolving the  $\text{Cu}_2\text{O}$  in the phospho-molybdate reagent, and titrating with  $\text{KMnO}_4$ , giving thereby much lower limits of measurement. Cu can be estd. by electrolyzing by Pregl's method, and immersing the cathode in some of the molybdo-phosphate reagent. The Cu dissolves rapidly. The soln. is titrated with  $\text{KMnO}_4$  as usual. A. T. CAMERON

**The use of the daylight lamp in volumetric and colorimetric analysis.** WM. SINGLETON. *Analyst* **47**, 424-6(1922).—Osram-G. E. W-filament type lamps fitted with "daylight" glass bulbs in 60, 100 and 200 watt sizes were used as a source of light in the comparison of results of titrations in artificial daylight, ordinary artificial light and natural daylight. Titrations were made using  $N/50$  acid and alkali solns. with the following indicators: thymol blue, acid and alkali range; bromophenol blue; methyl red; bromocresol purple; bromothymol blue; phenol red, cresol red, cochineal, Congo red, dimethyl aminoazo benzene, lacmoid, litmus, methyl orange, phenolphthalein and thymolphthalein. In most cases the color range was shorter and the end point more accurately observed in artificial than in natural daylight. "Spot" titrations using external indicators such as tannic acid when detg. Pb with  $(\text{NH}_4)_2\text{MoO}_4$  and K ferrocyanide in detn. of  $\text{H}_3\text{PO}_4$  with U titration were increased in accuracy by the use of artificial daylight. ARTHUR L. DAVIS

**The oxidimetric determination of calcium and its application to technical work.** J. GROSSFELD. *Chem. Weekblad* **20**, 39-41(1923).—It is recommended to dissolve the sample in 4  $N$   $\text{H}_3\text{PO}_4$  soln. and to ppt. the Ca as oxalate by adding a carefully measured vol. of 2%  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and an excess of NaOH soln. After filtering, the excess of oxalate is detd. by titration with  $\text{KMnO}_4$ . R. BRÜTNER

**Total and available calcium hydroxide in hydrated lime.** A. S. BEHRMAN AND F. R. PORTER. *Ind. Eng. Chem.* **15**, 269(1923).—When lime is used for water softening it is often found that the quantity of lime actually utilized in the softening process does not correspond to the total  $\text{Ca}(\text{OH})_2$  content as detd. by the usual methods. The following procedure is suggested for detg. more nearly how much lime is really available. Mix 1 g. of the unscreened lime with 100 cc. of boiled distd. water and allow to stand several hrs. to insure complete pptn. of  $\text{Mg}(\text{OH})_2$ . To the cold soln. add 100 cc. of 0.1  $N$   $\text{NaHCO}_3$  and allow to stand  $3\frac{3}{4}$  hrs. longer. Filter and titrate an aliquot part of the filtrate with 0.1  $N$   $\text{HCl}$ , phenolphthalein being used as indicator. W. T. H.

**The absorption and analysis of gaseous oxides of nitrogen.** A. SANLOURCHE. *Bull. soc. chim.* **31**, 1248-64(1922); cf. *C. A.* **17**, 36.—There has been considerable controversy, especially between Lunge and Raschig, with regard to the accuracy of results obtained in analyzing nitrous oxide mixts. and especially with regard to the use of alk. or acid absorbents. A series of careful expts. has confirmed the opinion previously expressed (*C. A.* **13**, 1055; **16**, 2464) that  $\text{H}_2\text{SO}_4$  is a better absorbent than an alk. medium. These expts. also indicate that  $\text{N}_2\text{O}_3$  actually exists in the gaseous phase and that this mol. takes a most active part in the absorption process. It is more difficult to explain the absorption on the basis of the theory that  $\text{N}_2\text{O}_3$  is merely a mixt. of NO and  $\text{NO}_2$ . As a result of secondary reactions, the use of alk. absorbents is likely to lead to quite erroneous results in analysis. It is also more difficult to accomplish complete absorption in some cases. W. T. H.

**The detection of nitric acid with ferrous sulfate.** C. FAURHOLT. *Ber.* **56B**, 337-41(1922).—The usual qual. test for  $\text{HNO}_3$  which depends upon the formation of

a brown ring of  $\text{FeSO}_4 \cdot x\text{NO}$  can be made more sensitive so that 0.2 mg. of  $\text{KNO}_3$  can be easily detected if a little  $\text{HCl}$  is added to the mixt. of substance and concd.  $\text{H}_2\text{SO}_4$  before adding the  $\text{FeSO}_4$  soln. Mix 2 cc. of the nitrate soln. with 4 cc. of concd.  $\text{H}_2\text{SO}_4$ , cool and add 1 drop of 4 *N*  $\text{HCl}$ . Then add a slightly acid 20%  $\text{FeSO}_4$  soln.

W. T. H.

**Hydrogen peroxide in Kjeldahl digestion for nitrogen.** SVEN LILJEVALL. *Svensk. Kem. Tids.* 34, 187-9(1923).—In the detn. of N by the Kjeldahl method  $\text{H}_2\text{O}_2$  is an effective supplement to the oxidizing agents. The  $\text{H}_2\text{O}_2$  is added before the  $\text{H}_2\text{SO}_4$ .

A. R. ROSE

**The volumetric determination of phosphoric acid and of sodium phosphate and pyrophosphates.** F. X. MORRIS. *Am. J. Pharm.* 94, 641-50(1922); cf. *C. A.* 16, 215, 4157.—Two methods depending upon neutralization are described, (1) with indicator, (2) in the presence of  $\text{AgNO}_3$ : (1) To 100 cc. distd.  $\text{H}_2\text{O}$  or other specified liquid, add 0.2 cc. each of the Me orange soln. (0.1 g. per 100 cc.) and indigo-carmin soln. (0.3 g. per 100 cc.); then add a dil.  $\text{HCl}$  soln. (about 0.1 *N*) drop by drop, until the green color changes without producing a violet color and divide the soln. into 2 equal portions, placing these portions in beakers of the same internal diam. (This procedure will ensure the same tint in both portions, whereas the directions previously given, namely, to add 0.1 cc. of each of the colored liquids to 2 portions of 50 cc.  $\text{H}_2\text{O}$  or other specified liquid, and treating these separately with  $\text{HCl}$ , often gave differently tinted solns.) To one of these portions add the soln. to be tested and titrate with  $\text{NaOH}$  until the color matches the reserved portion; for final decision in the matching hold the beakers over a white surface and look down through the liquids. If desired a check titration can next be made by adding another portion of the soln. to be tested to the reserved portion and matching this against the previously titrated soln. (2) Place a calcd. excess of 10%  $\text{AgNO}_3$  soln. which must be neutral (ensured by adding  $\text{NaOH}$  V. S. to the stock soln. of  $\text{AgNO}_3$  until a brown ppt. forms, allowing the ppt. to settle and decanting the clear soln.) in a beaker, add the soln. to be tested and then  $\text{NaOH}$  with const. stirring; as the yellow  $\text{Ag}_3\text{PO}_4$  becomes bulkier it will promptly settle so that part of the supernatant liquid can be decanted into another beaker and the titration continued; as the ppt. in this beaker increases, the mixt. is transferred back to the original beaker, thoroughly stirred, the liquid decanted and titration continued until finally one drop of  $\text{NaOH}$  produces a brown coloration not changing to yellow upon mixing with more of the supernatant liquid from the original beaker. The  $\text{AgNO}_3$  necessary can be calcd. from the wt. taken for assay or from the results of the neutralization method with indicator; one mol. of  $\text{H}_3\text{PO}_4$  or  $\text{Na}_2\text{HPO}_4$  or of  $\text{NaOH}$  or  $\text{HCl}$  requires 3 mols. of  $\text{AgNO}_3$ . Experience with the  $\text{AgNO}_3$  and  $\text{NaOH}$  method is not affected by variation in the several influences as in the indicator method and is suitable for  $\text{H}_3\text{PO}_4$  and mono- $\text{Na}$  and di- $\text{Na}$  phosphate; tri- $\text{Na}$  phosphate will give a neutral filtrate after the addn. of  $\text{AgNO}_3$  and therefore this method is not applicable.

W. G. GAESSLER

**Methyl red in the assay of phosphoric acid and sodium phosphate.** F. X. MORRIS AND E. J. HUGHES. *Am. J. Pharm.* 94, 650-5(1922).—The use of Me red as a suitable indicator for the  $\text{AgNO}_3$  and alkali V. S. method (preceding abstr.) was found to give better results than either the U. S. P. IX method or the mixed indicator method which gives the quickest results but is influenced by the wt. taken, the strength of the  $\text{NaCl}$  soln., the strength of the volumetric soln., and most seriously, by the detn. of the indigo-carmin soln. By using fresh indigo-carmin soln. and paying attention to the other factors mentioned, very satisfactory results are obtainable. From the work described in this and the preceding paper the following tabular arrangement shows the conditions for obtaining the best results with the mixed indicator.

$\text{H}_2\text{PO}_4$			$\text{Na}_2\text{HPO}_4$ dried.		
Wt. taken.	NaCl soln. *	Volumetric soln.	Wt. taken.	NaCl soln. *	Volumetric soln.
about 1. g.	7.5%	0.5 N	about 1. g.	2.5%	0.5 N
about 1. g.	10. %	0.2 N	about 1. g.	1. %	0.2 N
about 0.1 g.	10. %	0.1 N	about 0.2 g.	unnecessary	0.1 N

\*Interpret % NaCl soln. as g. per 100 cc.

W. G. GAESSLER

**The detection of fluorine in inorganic fluorides.** H. TER MEULEN. *Chem. Weekblad* 20, 59(1923).—In the presence of  $\text{H}_3\text{BO}_3$ , F cannot be detected in the usual way by heating with  $\text{H}_2\text{SO}_4$  owing to the formation of  $\text{BF}_3$  (similar to  $\text{SiF}_4$ ) which does not etch glass.

R. BEUTNER

**Pyrogallic acid solution for absorption of oxygen.** K. E. SKÄRBLOM. *Teknisk Tids. (Kemi)* 53, 3-4(1923).—Attention is called to the many recipes for pyrogallic acid-KOH mixts. used in absorption pipets. S. suggests that the proportions of the 2 components should be molar. Such a mixt. would be as follows: 15 g.  $\text{C}_6\text{H}_3(\text{OH})_3$ , 21 g. KOH, and 86 g.  $\text{H}_2\text{O}$ . This recipe has proved successful during two years and is more efficient than some of the many others used and is cheaper in that it contains less KOH than any of the others.

A. R. ROSE

**Estimation of water by the apparatus of Meihuizen.** K. MOHS. *Wochschr. Braueri* 39, 139-41.—Tests with Meihuizen's drying app. (Brit. pat. 114,820) are described. By using steam heat and maintaining a temp. of  $99^\circ$ , the moisture content of flours, starches, etc., may be detd. by heating for 50-60 mins. If xylene is used in place of water a drying temp. of  $139^\circ$  can be maintained and heating for 15-25 mins. is sufficient. Cf. C. A. 17, 904.

J. S. C. I.

**Analysis of pyrites.** E. J. VIRGIN. *Teknisk Tids. (Kemi)* 53, 1-4(1923).—This article is a detailed outline of the technic in the detn. of S in pyrites as followed in the Swedish and Norwegian labs. In the main it follows the classic Lunge procedure. The Fe is removed as  $\text{Fe}(\text{OH})_3$  and dissolved in dil. HCl and this soln. is treated with  $\text{BaCl}_2$ . If a ppt. forms this is added to the  $\text{BaSO}_4$  ppt. from the  $\text{Fe}(\text{OH})_3$  filtrate. A modification is used (Gyzander's method) in which the Fe is not removed but at this step  $\text{NH}_4\text{OH} \cdot \text{HCl}$  and  $\text{NH}_4\text{Cl}$  are added. (20 cc. of a soln. contg. 20 g.  $\text{NH}_4\text{OH} \cdot \text{HCl}$  and 100 g.  $\text{NH}_4\text{Cl}$  per l.) When the soln. is now heated as for  $\text{BaSO}_4$  pptn. the Fe is reduced and is not occluded by the  $\text{BaSO}_4$  ppt.

A. R. ROSE

**Separation of iron and zinc by means of bases.** K. SCHERINGA. *Pharm. Weekblad* 60, 39-43(1923).—A complete sepn. can be effected in one operation by pptg. the  $\text{Fe}^{+++}$  with excess of 25%  $\text{NH}_4\text{OH}$  and washing the pptd.  $\text{Fe}(\text{OH})_3$  with  $\text{NH}_4\text{OH}$  of the same concn. Evap. the soln., which should not contain more than 150 mg.  $\text{Fe}_2\text{O}_3$ , to about 10 cc. If much Zn is present add 25 cc. of 25%  $\text{NH}_4\text{OH}$ , filter cold and wash with  $\text{NH}_4\text{OH}$  of the same concn. If only a small amt. of Zn is present 10%  $\text{NH}_4\text{OH}$  may be used. After removal of free and combined  $\text{NH}_3$ , Zn may be detd. in the filtrate.

A. W. DOX

**The determination of abietic acid and of rosin.** F. SCHULZ AND S. LANDA. *Bull. soc. chim.* 31, 1353-60(1922).—In studying the isomerism of the abietic acids extd. from Am. rosin, it was found that these acids give an abundant ppt. of  $\text{AcOHg}$  when treated at  $60^\circ$  with an AcOH soln. of  $(\text{AcO})_2\text{Hg}$ . The Hg in the ppt. can be easily titrated by the method of Votocek (C. A. 12, 2177). In this way the rosin content of mixts. can be detd. within 10% of the truth which is about as accurate as any other method that has been proposed for such analysis. Dissolve 0.5 g. of the substance in 10 cc. of glacial AcOH which is satd. with AcOHg. After the substance has dissolved, add 50 cc. of  $\text{Hg}(\text{AcO})_2$  soln. prepd. by dissolving 3 g.  $\text{HgO}$  in AcOH which is satd. with AcOHg. Heat on the water bath for 1 hr. at  $50^\circ$  and then allow to stand an hr. protected from light. Collect the lustrous crystals on an asbestos filter which has been moistened with

AcOH satd. with AcOHg and wash with AcOH satd. with AcOHg. Dissolve the ppt. in 20 cc. of hot, 20%  $\text{HNO}_3$  and wash the filter with boiling water until the filtrate will give no test for Hg with  $\text{SnCl}_2$  soln. Add 20 cc. of concd.  $\text{H}_2\text{SO}_4$  with an excess of  $\text{KMnO}_4$  and boil 20 min. to oxidize the mercurous salt. Destroy the excess  $\text{KMnO}_4$  with a little  $\text{H}_2\text{C}_2\text{O}_4$  and allow the soln. to cool. Then add 50 cc. of standard NaCl soln. (13 g. per l.), a little Na nitroprusside and titrate the excess NaCl with a soln. of  $\text{Hg}(\text{NO}_3)_2$  until a permanent ppt. is produced. (24.2 g. of HgO dissolved in  $\text{HNO}_3$  and dild. to 1 l. should correspond exactly to a soln. of NaCl contg. 13 g. per l.) One cc. of the NaCl soln. corresponds to 0.241 g. of HgO or to 0.0131 g. of rosin. The reducing power of the abietic acid in AcOH changes on standing.

W. T. H.

**Detection of diethyl phthalate and phthaleins.** R. L. CALVERT. *Am. J. Pharm.* **94**, 702-3(1922).—The test described by Lyons (*C. A.* **16**, 1634) is not satisfactory, especially if diethyl phthalate (A) is present in minute amts. C. describes a delicate test, depending upon the formation of phenolphthalein by the action of hot  $\text{H}_2\text{SO}_4$  on phenol and A to detect the presence of A or a phthalein in EtOH. To 3 or 5 cc. of the sample in a test-tube add 5 to 10 drops of phenol, 10 drops of concd.  $\text{H}_2\text{SO}_4$  and heat slowly over a small Bunsen flame until most of the EtOH has been driven off and the liquid assumes a red color. Cool and cautiously add 15-25 cc.  $\text{H}_2\text{O}$ ; the red color will disappear and the liquid become turbid (if positive). Add an excess of NaOH or KOH. A red color denotes the presence of A or a phthalein in the sample.  $\text{NH}_4\text{OH}$  is not recommended owing to the possible formation of phenoldiiminophthalein, a substance giving a colorless soln. with alkalis.

W. G. GAESSLER

**The determination of acetone in methanol.** ELLA SÖDERLUND. *Svensk Kem. Tids.* **34**, 152-7(1922).—When acetone is titrated with 0.1 N I soln. it is important to add the I soln. rapidly and to use 100% of it in excess and then place the flask in a dark closet. When the reaction is judged to be complete add 1.0 N  $\text{H}_2\text{SO}_4$  and titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . A sample contg. 0.1% acetone will react as if it contained 0.2% if the sample is allowed to stand in dull light for 25 min. and 1% if placed in direct sunlight.

A. R. ROSE

Ultra-violet luminescence in legal medicine (STOCKIS) 11B.

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

**Phosgenite from the Terrible Mine, near Ilse, Custer Co., Colorado.** W. A. WALDSCHMIDT. *Am. Mineral.* **8**, 31-3(1923).—Phosgenite occurs in smoky transparent masses associated with cerussite. It contained 75.3% Pb and gave blowpipe tests for Pb,  $\text{CO}_2$ , and Cl. Sp. gr. = 6.08.

E. F. H.

**A correction: Recently described crystals of glaucocroite from Franklin, N. J. are tephroite.** S. G. GORDON. *Am. Mineral.* **8**, 33-4(1923).—The ms. of the crystals are  $\alpha$  1.765  $\pm$  .005,  $\beta$  1.78  $\pm$  .01,  $\gamma$  1.79  $\pm$  .01 (Larsen). Two of the forms described are new for tephroite:  $j$ (270) and  $q$ (122).

E. F. H.

**Recently found meteoric iron from Glasgow, Barren County, Kentucky.** G. P. MERRILL. *Am. J. Sci.* **5**, 63-4(1923).—Two pieces of this meteorite were found in plowing a field. The smaller piece, weighing 15.25 lbs., was sent to the Nat. Museum. It is a coarse octahedrite; no troilite nodules are visible on the cut surface, neither taenite nor schreibersite are conspicuous, and plessite areas are small. The Fe is in an advanced condition of oxidation that is difficult to arrest, suggestive of a high content of lawrencite. Analysis by Whitfield gave: Fe 70.632, Ni 7.27, Co 0.62, S 0.11, P 0.121, C 0.062, Cl 0.363, NiFe oxides 19.22,  $\text{SiO}_2$  trace, ignition 1.65, sum 100.048%.

The high Cl figure, equiv. to 0.623% FeCl<sub>2</sub>, doubtless accounts for the ready disintegration.

L. W. RIGGS

**Geology and ore deposits of Salmon River district, British Columbia.** S. J. SCHOFIELD AND G. HANSON. Can. Dept. Mines, *Memoir* 132, 1-62(1922).—The geological features of the region are described in 34 pages. Since 1914 the Premier mine has reached a daily output of 500 tons of high-grade ore. Ores of similar grade occur in other parts of the district. The ores are classified as (1) low-grade siliceous type with values in Cu, Pb and Zn, (2) high-grade Ag-Au type, (3) pyritic siliceous type with high Au values. The origin, mineralogy and secondary enrichment of the ores are described. The most favorable associations for the occurrence of the ores are (1) in quartz porphyry, (2) at the contact of (1) with the tuffs, (3) in certain beds of the tuffaceous conglomerate. The slates do not appear favorable for the deposition of ores.

**Ore deposits of British Columbia.** S. J. SCHOFIELD. *Ibid* 63-73.—A general sketch of the work of the Can. Geol. Survey in B. C. is given, covering an exploratory period 1871-1905 and an intensive study period 1905-1921. The genesis of ore deposits and the modes of enrichment of ores are emphasized.

L. W. RIGGS

**Economic application of zonal theory of primary deposition of ores.** J. C. ANDERSON. *Trans. Am. Inst. Mining Met. Eng.* 1209M, 9 pp.(1923).—In general magnetite and hematite form first and are representative of the deeper zone; above and with them comes a zone of garnet, epidote and pyroxene, next bornite and chalcocopyrite; pyrrhotite-arsenopyrite; sphalerite; galena; Ag sulfides and Au. At the Magma Mine in Pinal County, Arizona, bornite and chalcocopyrite have been deposited below a sphalerite zone, and above all is a zone of Ag ores.

W. H. NEWHOUSE

**Manganese deposits of Lunenburg County, Nova Scotia.** F. C. FEARING. *Eng. Mining J. Press* 115, 11-5(1923).—The minerals present are manganite, pyrolusite, calcite and limonite. The ore bodies are small and lie along fault planes. The ores are secondary and were formed by surface water leaching.

W. H. NEWHOUSE

**The occurrence of copper at Alghero in Sardinia.** F. AHLFELD. *Glückauf* 58, 1507-13(1922).—The deposits are described mineralogically and geologically, with maps. The ores contain 7-26.5% Cu, averaging 9.5%, and consist of several veins between Triassic limestones and a massif of dacite. The veins contain Cu pyrite, Cu glance and covellite. They were probably formed in conjunction with the upheaval of dacite magma, and originated by hydrothermal metasomatism (cf. Ciampi, Note geologico-minerarie sui giacimenti cupriferi della regione di Alghero, *Boll. Assoc. Min. Sarda* 1922).

C. C. DAVIS

**Mercury in New Zealand.** T. A. BLACK. *Chem. Eng. Mining Rev.* 15, 17-9 (1922).—The com. deposits are located in the Puhipuhi district 25 miles north of Whangarei. Hydrothermal deposition of quartz and cinnabar along a fault plane has formed the ore deposits.

W. H. NEWHOUSE

**Porcelain clays of Ballerat.** R. C. CALLISTER. *Chem. Eng. Mining Rev.* 15, 36-43(1922).—The clays occur in sedimentary beds 6 feet thick at Lal Lal and Bachus Marsh. Also as residual deposits on granite at Lal Lal. A relatively high content of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> is present.

W. H. NEWHOUSE

**Geology of the Moncton map-area.** W. J. WRIGHT. Can. Dept. Mines, *Memoir*, 129, 60 pp.(1922).—A geological description fills 28 pages. The remainder of the paper is devoted to the oil shales of this area and to those of Nova Scotia. Analyses of 43 samples of 20 lbs. each of shales from Albert Co., N. B. are tabulated. Excluding 2 barren samples the ash content ranges from 63.0 to 83.5%, B. t. u. per lb. 630 to 4200, av. about 1600, N 0.21 to 0.71%, yield of oil per ton 4.8 to 32.2 imp. gal., yield of gas per ton 380 to 1485 cu. ft. The B. t. u. per cu. ft. of the gas ranged from 280 to 770. Fifty tons of shale from the Baltimore, N. B., area was sent to Scotland and retorted



by the Pumpherson Oil Co. The results of this test were: oil per ton 40.0 imp. gal. with a sp. gr. of 0.92,  $(\text{NH}_4)_2\text{SO}_4$  per ton 77.0 lbs. Five other samples from this area gave from 39.0 to 56.8 imp. gal. of oil and 30.5 to 112.2 lbs. of  $(\text{NH}_4)_2\text{SO}_4$ , resp., per ton. Five samples of shale from New Glasgow, N. S. gave from 2.3 to 14.7 imp. gal. per ton.

L. W. RIGGS

**Raphaelite; its genetic relation to certain Argentine coals and petroleum.** ERNESTO LONGOBARDI. *Anales asoc. quim. Argentina* 10, 215-9(1922).—Raphaelite is a carbonized asphalt mineral resembling coal. It is evidently related to neighboring deposits of highly asphaltic petroleum as both it and the petroleum are rich in S and contain traces of V compds. Other more remote Argentine petroleum deposits contain no V. There are in Argentina other deposits of so-called coal which are similar to raphaelite. All of these "coals" yield acid vapors when subjected to destructive distn.

L. E. GILSON

**What lies beneath granite?** HANS CLOOS. *Naturwissenschaften* 11, 7-10(1923).—A discussion with new evidence. The general assumption that granite is the substratum of all other rocks is rendered improbable by a study of the granite massifs in the Bavarian forests. Granite occurs with all the typical geologic features of batholiths, but it does not penetrate deep and rests on a non-granite substratum. The latter is composed of gneiss and lies under the granite with its contact surface mainly in a horizontal plane.

C. C. DAVIS

**Fire damp in the gold mines of the Far East Rand.** T. N. DEWAR. *J. Chem. Met. Soc. S. Africa* 21, 127-34(1921).—Fire damp was present 4000 ft. deep in Au mines. The gas was usually in or about the footwall shales, with free C occasionally at the contact of the reef and shale. In the majority of cases, faulting and  $\text{H}_2\text{O}$  seemed necessary for the presence of fire damp.  $\text{H}_2\text{S}$  was occasionally present. Heat causes a reaction between pyrite,  $\text{H}_2\text{O}$  and C in and under the shale and there is probably faulting from overlying coal down to the Au measures. Dolomite contg.  $\text{H}_2\text{O}$  in its crevices forms such a channel.

C. C. DAVIS

**Investigation of terrestrial gases. II.** F. HENRICH AND G. PRELL. *Ber.* 55B, 3021-5(1922); cf. *C. A.* 15, 355.—The method of collecting for analysis samples of gas from springs has been improved. A glass bulb provided with a long tip is evacuated and sealed off. The end of this tip is broken off in a rubber tube leading to a funnel immersed in the spring water. When the tube has filled the tip is again sealed off above the rubber tube and taken to the lab. for analysis. The ratio of the inert gases to N in radioactive gases from certain springs is greatly different from that in ordinary air. **III.** *Ibid* 3026-30.—Analyses of 5 samples of gas obtained from the bottom of pools of water showed traces of  $\text{H}_2\text{S}$ , 0.1-2.7%  $\text{O}_2$ , 30.9-61.4%  $\text{CH}_4$ , and 35.8-67.9% ( $\text{N}_2$  + inert gases).

D. MACRAE

**Manchurian magnesite (HIRANO) 19.** Determination of the specific heats and specific weights of several minerals (DANNHOLM) 2.

## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

**Accidents at metallurgical works in the United States during 1921.** WM. W. ADAMS. *Bur. of Mines, Tech. Paper* 327, 30 pp.(1923).

E. J. C.

**Heap leaching at Bisbee, Arizona.** A. W. HUDSON AND G. D. VAN ARSDALE. *Trans. Am. Inst. Mining Met. Eng.*, Preprint No. 1212-M, 16 pp.(1923).—An account of preliminary test work by the Phelps Dodge Corp'n. and of the proposed treatment of low-grade ore removed by stripping.

E. J. C.

Gold and silver in 1921. J. P. DUNLOP. U. S. Geol. Survey, *Mineral Resources of U. S. 1921*, Pt. I, 429-66 (preprint No. 26, publ. Jan. 26, 1923). E. J. C.

Metallurgical possibilities of the descloizite ores at Goodsprings, Nevada. H. A. DOERNER. Bur. of Mines, *Repts. of Investigations* No. 2433, 19 pp. (1923).—The district is capable of producing 2.5 tons per day of ore averaging 2-3%  $V_2O_5$ . A concg. mill is essential for the exploitation of the deposits as ore of the above concn. will not stand the cost of shipping or of chem. refining. Classification and tabling of the ore and treatment of the slimes will ext. 70% of the Pb and V content and yield a concentrate with 10%  $V_2O_5$  and over 30% Pb. This may be shipped or further refined. The procedure for refining is an alk. fusion, sepn. of Pb from slag, digestion and neutralization with  $H_2SO_4$ , the vanadic acid pptg. Complete tests on this and other methods are given. C. H. HERTY, JR.

Pyritic smelting and basic converting at the Kosaka Copper Smelter, Japan. K. IKEDA. *Trans. Am. Inst. Min. & Met. Eng.* No. 1204-N, 9 pp. (1923).—Pyritic smelting is satisfactorily conducted with a charge column only 9 ft. high by introducing nut coal through the tuyères. Magnesite-brick linings in converters give remarkable service through the Fe-bearing coating formed in them. This coating analyzes 74.75%  $Fe_2O_3$  and melts about 75° higher than the temp. of the converter bath, though in some cases it may be slightly lower. The high cond. of the magnesite allows the coating to reform rapidly. C. H. HERTY, JR.

Losses of lead during the smelting of low-grade material. C. OFFERHAUS. *Metallic u. Erz* 18, 591-7 (1921).—Details are given of the losses of lead during 3 weekly runs of a lead blast furnace charged with a mixt. of low-grade lead ores, rich slag (8.5% Pb), and broken cupels. The av. assays of the charges were 11.4, 12.5, and 15.1% Pb, and losses were 17.4, 14.6, and 10.9%, resp., the greater part of which went into the slag. The losses in fume were about 12.5% of the total loss, and the slag contained 1.4-1.75% Pb. Direct smelting of the rich slag contg. 8.5% Pb resulted in an unavoidable loss of 19% of the total lead. It is suggested that the formula for buying ores based on the assay figures should be considerably modified for low-grade material owing to the relatively higher losses that ensue during smelting. J. S. C. I.

Malleable-iron metallurgy. M. M. MARCUS. *Foundry* 50, 994-5 (1922).—Owing to lower C and Si contents and consequent higher m. p., cast iron for malleablizing must be poured more rapidly and at a higher temp. than gray iron. This is also necessary to hold the C in soln. There is greater shrinkage and greater liability to crack. Initial contraction is double that of gray iron, and amounts to  $1/4$  in. to the ft. On annealing there is an expansion of  $1/8$  in. to the ft. Cracks often do not show until after annealing. Chem. analysis is important. The effect of varying amts. of C, Si, and Mn is discussed, and data are given on annealing. A. BUTTS

Aluminium melting practice. R. J. ANDERSON. *Foundry* 50, 823-9, 866-70, 919-24 (1922).—The use of molten flux covers in Al melting will reduce oxidation and gas adsorption, but such use is not widely practiced. Salts sometimes used for covers are KCl, cryolite, NaCl, borax,  $CaF_2$ , LiF,  $Na_2CO_3$ , and various mixts. of these. Rapid melting and prompt pouring of A are essential to reduce oxidation. The amt. of dissolved gas and dross loss is a function of the temp., time, and compn. of the furnace atm. Heat may be conserved by filling the furnace with metal after the last pour at night, as the metal charge will cool more slowly than an empty furnace. Use of borings and scrap in charges increases drossing. Melting pots or crucibles are usually of cast Fe or plumbago. Molten Al rapidly attacks steel, and will also reduce Si and other elements from refractories, with formation of  $Al_2O_3$ . Iron pots last 8-12 days with 9-12 hrs. use per day. Washes of cement, fireclay, lime, etc., prolong the life of both pots and crucibles. The choice of a refractory is important in melting furnaces where

there is contact between the Al and the hearth or lining. Fireclay is most common, but various others are used. Various types of furnaces are used. The Fe pot seems to be preferred, and is the only one not also used for brass and bronze. The best choice depends on the material—whether Al metal or alloy—and the type of ingot or casting to be made. The tendency is toward furnaces of higher capacity, especially in large foundries. One open-flame barrel-type melts 2000 lb. per hr. Fe-pot furnaces are either stationary or tilting. Design, operation, and fuel are discussed in detail for the various types of furnaces, and compilations of 60 replies to a questionnaire on details of Al foundry practice are given. Cf. C. A. 16, 1384, 3861; 17, 373. A. BUTTS

**Handling malleable castings in process.** F. L. PRENTISS. *Iron Age* 111, 591-4 (1923). E. J. C.

**Open-hearth steel practice.** WILLIS MCKEE. *Foundry* 50, 990-3 (1922).—Combustion that is imperfect or delayed until after the gases have passed over the charge is the greatest cause of low thermal efficiency, and also causes damage to uptakes, slag pockets, and regenerators from overheating. The blow-torch principle, using ports of such design that the air and gas mix before entering the hearth chamber, obviates this trouble. The entering velocity must be high to keep down combustion in the ports. The melting time is greatly shortened. In using this method it is proposed to dispense with gas regenerator chambers when producer gas is used, and to make the gas near the furnace and conduct it through insulated steel mains. This would simplify construction and should give additional fuel economy. Design of ports is discussed, with diagrams. A. BUTTS

**Copper-antimony alloys.** N. S. KURNAKOV AND K. F. BYELOGLAZOV. *Rev. soc. phys. chim. Russe; Rev. métal.* 19, 588-9 (Abs.) (1922).—After reviewing results obtained by themselves (cf. C. A. 11, 3153) and by Reimann (C. A. 15, 1124), K. and B. comment as follows. The at. ratio of Cu and Sb observed by Reimann, and by K. and B., and calcd. for  $\text{Cu}_5\text{Sb}_2$  and for  $\text{Cu}_5\text{Sb}$  are 2.45:1, 2.57:1, 2.5:1 and 3:1, resp. The 2 sets of exptl. results are very concordant, but Reimann's conclusion that phase  $\beta_2$  belongs to the definite compd.  $\text{Cu}_5\text{Sb}_2$  is not in accordance with the properties of the substance as a whole. Within the range where it is stable,  $\beta_2$  shows a singular point neither on the fusibility diagram nor on the elec. cond. isotherms and temp. coeff. isotherms at 400-600°. A. P.-C.

**Babbitt metals. Their character and uses.** L. D. ALLEN. *Raw Material* 6, 56 (1923). E. J. C.

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Trend in blast-furnace gas cleaning (KLING) 21. Process in the stretching of Zn crystals (MARK, *et al.*) 2. Fluorspar in steel manufacture (JONES) 18. Determination of the specific gravity and specific heat of antimony-lead alloys (LINNAVUORI) 2.

**Converting ores and concentrates into sulfates.** J. B. READ AND M. F. COOLBAUGH. *Can.* 228, 141, Jan. 23, 1923. Sulfide ores of Fe and at least one of the metals Cu, Pb and Zn are roasted at 600-1000°, the temp. is lowered to a temp. at which  $\text{CuSO}_4$  is stable and the product and gases contg. oxides of S are passed in the same direction through the furnace throughout the entire process.

**Ore grinding and concentrating apparatus.** J. O. THOMAS. U. S. 1,444,485, Feb. 6.

**Ore flotation.** C. M. NOKES. U. S. 1,444,552, Feb. 6. Finely divided non-sulfide ores such as oxidized Cu ore or Ag ore contg. Mn are prepd. for flotation sepn. by treatment with a mixt. of Na sulfide, paraffin and pine oil.

**Ore flotation apparatus.** J. P. RUTH. U. S. 1,445,042, Feb. 13.

**Roasting zinc sulfide ores.** H. W. GEPP. U. S. 1,443,707, Jan. 30. In roasting ZnS ore preparatory to leaching, the S content of the ore is first brought to about 6-10%.

of the wt. of the ore as usual and the roasting is then continued at a low temp. (preferably about 725°) in the presence of an air supply which is controlled to cause a max. sulfate production. U. S. 1,443,708 specifies a similar process in which such quantities of green sulfide ore are added at intervals during the roasting as to bring the sulfide S content of the material up to about 2% after each addition.

**Extracting copper from its ores.** P. W. NEVILL and H. SOANES. Can. 228,117, Jan. 16, 1923. A pulp is made of the crushed ore and a dil. acid or salt soln. insufficient in amt. to dissolve the Cu content of the pulp; the pulp is agitated with a reducing agent such as finely divided Fe to change the Cu to cement Cu, which is then sepd. from the gang.

**Cartridge for refining molten metals.** A. H. LEVY. U. S. 1,443,920, Jan. 30. A cartridge of flux is carried on a holder by which it may be immersed in molten type metal or other metal.

**Sintering flue dust.** T. J. DAVIS. U. S. 1,444,955, Feb. 13. A porous hearth of coarse sintered material is covered with flue dust to be sintered and the bed thus formed is ignited.

**Metallurgical furnaces.** B. TALBOT. Can. 227,651, Jan. 2, 1923. Structural features of a tilting regenerative furnace that can be continuously operated.

**Ore-roasting furnace.** R. D. PIKE. U. S. 1,444,209, Feb. 6. The furnace is adapted for roasting Cu ores. It comprises an outer stationary shell, a vertical rotary shaft centrally located within the shell, spaced horizontal hearths within the shell each provided with outlets for material, hollow rabble arms carried on the shaft with a covering of refractory and insulating material and connections for supplying cooling air.

**Circular, superposed-hearth, rabble furnace for roasting ores.** A. V. LÖGGO. U. S. 1,444,927, Feb. 13.

**Gas- or oil-fired furnace for heating ingots or billets of metal.** C. W. HEPPENSTALL. U. S. 1,444,918, Feb. 13.

**Sponge iron.** E. P. THORNHILL. U. S. 1,443,444, Jan. 30. Particles of Fe oxide and a reducing agent such as powdered coal, coke or a hydrocarbon oil are showered through a heated retort in a reducing atm. at such a temp. as to effect reduction of the oxide particles to sponge Fe and the shower of particles is cooled during their fall subsequently to a temp. below that of agglomeration.

**"Stainless steel."** F. D. CARNEY. U. S. 1,444,062, Feb. 6. Ferrochrome is added to steel and the melt is maintained sufficiently hot to cause selective oxidation of the Cr rather than the Fe and produce a "stainless" alloy steel.

**Safe or vault plate.** O. HUTCHINS and C. E. HAWKE. U. S. 1,444,610, Feb. 6. Refractory fragments contg. at least 97% of  $Al_2O_3$  are embedded in cast Fe or steel or similar cast metal forming the matrix of safe or vault plates which are resistant to the oxy-acetylene flame.

**Refractory metal alloys.** B. D. SAKLATWALLA and A. N. ANDERSON. Can. 228,287, Jan. 23, 1923. In the reduction of V-contg. materials in an elec. furnace a molten bath having a slag layer is moistened on the hearth and the electrodes extend into the layer. A mixt. of the V material, a carbonaceous material and, if necessary, a flux is fed directly into the high-temp. reaction zone of the furnace.

**Acid-resisting alloy.** R. WALTER. U. S. 1,444,891, Feb. 13. An acid-resisting Fe alloy which may contain Si 13–25% and C 0.65% or more is formed by melting down the ingredients and is poured at a temp. only slightly above the fusing point of the alloy, in order to prevent Si cementite from forming.

**Soldering flux.** A. L. BROWN. U. S. 1,444,946, Feb. 13. Resinate of Zn is used with fat,  $NH_4Cl$  and glycerol in fluxes for soldering.

## 10—ORGANIC CHEMISTRY

CHARLES A. ROULLER

**Designation of steric series.** A. WOHL AND K. FREUDENBERG. *Ber.* 56B, 309-13 (1923); cf. Freudenberg, *C. A.* 16, 3871; Wohl, *C. A.* 16, 3873.—W. and K. agreed as to exptl. results in the earlier papers but differed as to the use of the terms *d* and *i* and + and —. They now give rules for the designation of steric series. The original should be read for these rules.

C. J. WESS

**Absorption of ethylene by sulfuric acid. Production of ethyl alcohol, diethyl sulfate and liquid hydrocarbons.** A. DAMIENS. *Bull. soc. chim.* 33, 71-81(1923).—*See C. A.* 17, 259.

E. J. C.

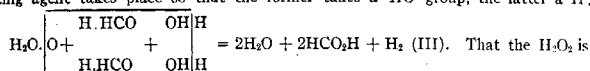
**Decomposition of ethers by metallic sodium.** PAUL SHORIGIN. *Ber.* 56B, 178-86 (1923).—Aromatic and fatty-aromatic ethers, boiling above 200°, are readily decompd. by boiling with Na in an open vessel, while lower-boiling ethers must be heated in a sealed tube. Fatty ethers showed little decompn. at 275°. Ph<sub>2</sub>O began to react with Na at 180°. 20 g. gave 2-3 g. C<sub>6</sub>H<sub>6</sub>, 6-8 g. PhOH, 0.7 g. Ph<sub>3</sub>, 2 g. pitch, 3 g. charred material and about 0.8 g. higher phenols(?). Heated in 30 cc. C<sub>6</sub>H<sub>5</sub>Me<sub>2</sub> for 4 hrs. at 145-60°, only traces of PhOH were obtained; with iso-Am<sub>2</sub> 1 g. PhOH and with C<sub>10</sub>H<sub>8</sub> 3.5 g. C<sub>6</sub>H<sub>6</sub> and 6.5 g. PhOH. Passing dry air through the mixt. gave 2.7 g. C<sub>6</sub>H<sub>6</sub>, 3.5 g. PhOH and much C. With CO<sub>2</sub> 1 g. C<sub>6</sub>H<sub>6</sub> and 3.5 g. o-HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H were isolated. α-C<sub>11</sub>H<sub>21</sub>OEt and Na begin to react at 200°; after heating 2 hrs. at 250-80°, 3.2 g. C<sub>10</sub>H<sub>8</sub> and 4.7 g. α-C<sub>10</sub>H<sub>17</sub>OH were isolated. In 1 expt. C<sub>3</sub>H<sub>8</sub> was isolated as C<sub>2</sub>H<sub>5</sub>Br<sub>2</sub> (8 g.). Analysis of the evolved gases showed 0.044 mol. C<sub>2</sub>H<sub>6</sub>, 0.023 mol. C<sub>2</sub>H<sub>4</sub> and 0.012 mol. H. β-C<sub>10</sub>H<sub>20</sub>OEt decomps. even more readily than the α-deriv. 2 g. C<sub>10</sub>H<sub>8</sub> and 9 g. β-C<sub>10</sub>H<sub>17</sub>OH were isolated while the evolved gases analyzed 0.032 mol. C<sub>2</sub>H<sub>6</sub>, 0.021 mol. C<sub>2</sub>H<sub>4</sub> and 0.006 mol. H. PhOHt and Na were heated in a sealed tube several hrs. at 200-65°. 7 g. ether gave 1 g. PhOH, a very small amt. of EtOH, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and H. The decompn. of PhCH<sub>2</sub>OEt by Na begins at 140°. PhCH<sub>2</sub>OH was isolated but the other products were lost. Heating Na and (iso-Am)<sub>2</sub>O at 200-20° in a sealed tube for 10 hrs. caused a slight decompn. of the ether with the formation of some iso-AmOH. This work shows that it is not permissible to purify high-boiling ethers by distg. over Na. They should at most be heated to 100-20°, decanted from the Na and then distd. C. J. W.

**Synthesis of halogen compounds of the butane series.** JULIUS V. BRAUN AND GEORGE LEMKE. *Ber.* 55B, 3526-36(1922).—The 1,5-dihalogen derivs. of the pentane series can be prep'd. in good yields, but the 1,4-dihalogen compds. of the butane series have been difficult to prep. The new com. synthesis of cyclohexanol by reduction of phenol has opened a new method of prepn. Cyclohexanol is oxidized to adipic acid, whose amide is converted into 1,4-diaminobutane. Benzoylation and treatment with PBr<sub>3</sub> or PCl<sub>5</sub> yield the desired 1,4-dihalobutane. Bromination of 1,4-dibromobutane with 1 mole Br causes at. rearrangement to give 1,2,3-tribromobutane; energetic bromination gives 1,2,3,4-tetrabromobutane. Cyclohexanol oxidized with KMnO<sub>4</sub> yields 70% adipic acid, which is converted to the acid chloride by SOCl<sub>2</sub>, and to the amide in 90% yield. Conversion to the diamine by the Hofmann reaction and conversion to the di-Bz deriv. by the Schotten-Baumann method give 60% of the theory of synthetic dibenzoylputrescine, m. 176-7°. Warming with PBr<sub>3</sub> yields 70% of the theory of 1,4-dibromobutane, b<sub>4</sub> 80-2°. Disaccharyl tetramethylene, m. 204-6°, is obtained by reaction of 1,4-dibromobutane with Na saccharin.

E. H. VOLWILER

**Action of hydrogen peroxide on formaldehyde. Theory of oxidation processes.** A. BACH AND A. GENEROSOV. *Ber.* 55B, 3560-6(1922).—The known reactions of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O indicate that they react to form HCO<sub>2</sub>H and water through an addn. product: CH<sub>2</sub>O + H<sub>2</sub>O<sub>2</sub> = H<sub>2</sub>C(OH).O.OH = HCO<sub>2</sub>H + H<sub>2</sub>O (I). The reaction is

much more complicated, however. It has been shown [Ber. 31, 2979(1898)] that in the presence of alkali, 2 mols.  $\text{CH}_2\text{O}$  combine with 1 mol.  $\text{H}_2\text{O}_2$ , 1 mol.  $\text{H}_2$  being evolved:  $2\text{CH}_2\text{O} + 2\text{KOH} + \text{H}_2\text{O}_2 = 2\text{H.COO}_2\text{K} + 2\text{H}_2\text{O} + \text{H}_2$  (II). Caustic alkalis in certain concns. cause oxidation of  $\text{CH}_2\text{O}$  to  $\text{HCO}_2\text{H}$ , with evolution of  $\text{H}_2$ ; in other cases they cause rearrangement and condensation. B. and G. found that pure  $\text{CH}_2\text{O}$  and  $\text{H}_2\text{O}_2$  follow reaction II, the reaction rate being higher with increase of concn. and temp. The paradoxical evolution of  $\text{H}_2$  is explained in two ways by Traube and by Wieland. Since the methylene group is not affected, the  $\text{H}$  must come from the  $\text{H}_2\text{O}_2$  or from water. Since  $\text{H}$ -free oxidizing agents, such as  $\text{K}_2\text{CrO}_4$ , etc., also set free  $\text{H}_2$ , the latter does not come from the  $\text{H}_2\text{O}_2$ . Traube's theory is that since no oxidation takes place in absence of water, the reaction between the oxidizable substance and the oxidizing agent takes place so that the former takes a  $\text{HO}$  group, the latter a  $\text{H}$ :



not attacked by the nascent  $\text{H}$  must then be due to the production of mol.  $\text{H}_2$  more rapidly than reduction of the  $\text{CH}_2\text{O}-\text{H}_2\text{O}_2$  complex by  $\text{H}$  can proceed. This theory is supported by the observation of Legler (Ber. 18, 3347(1885)) that hexaoxymethylene triperoxide,  $(\text{CH}_2\text{O})_3\text{O}_3 \cdot 3\text{H}_2\text{O}$ , reacts with water according to II to yield  $\text{HCO}_2\text{H}$ , water, and  $\text{H}_2$ . According to Wieland's dehydration theory, water adds to  $\text{CH}_2\text{O}$ , which then is oxidized by  $\text{H}_2\text{O}_2$ :  $\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CH}_2(\text{OH})_2$ ;  $\text{CH}_2(\text{OH})_2 + \text{H}_2\text{O}_2 = \text{HCO}_2\text{H} + 2\text{H}_2\text{O}$ . To explain the production of  $\text{H}_2$ , part of the aldehyde hydrate must react:  $2\text{CH}_2(\text{OH})_2 + \text{H}_2\text{O}_2 = 2\text{CH}(\text{OH})_2 + \text{H}_2\text{O}$ ;  $2\text{CH}(\text{OH})_2 = 2\text{CH}_2\text{O}_2 + \text{H}_2$  (IV). Traube's theory can explain every case of oxidation by the  $\text{O}$  of  $\text{H}_2\text{O}_2$ , with evolution of  $\text{H}_2$ , whereas Wieland's theory cannot. Furthermore, Wieland's theory gives no clearer insight into the mechanism of the reaction than Traube's does. Wieland's application of his theory to biologic oxidation and reduction is also open to question; he believes that oxidation and reduction enzymes are identical, but B. was unable to cause reduction by purified peroxidase. B. and G. found that in the absence of alkali,  $\text{H}_2\text{O}_2$  and  $\text{CH}_2\text{O}$  will not react to completion, because of the  $\text{HCO}_2\text{H}$  produced. Excess  $\text{H}_2\text{O}_2$  causes the reaction to go partly according to I and partly according to II. E. H. VOLWILER

**Formation of geometrical isomers in the reduction of acetylene derivatives.** JUL. SALKIND. Ber. 56B, 187-92(1923).—The reduction of  $[\text{Me}_3\text{C}(\text{OH})\text{C}]_n$  with  $\text{H}$  and colloidal  $\text{Pd}$  gives *tetramethylbutenoglycol*, isolated in 2 forms:  $\alpha$ -form (A), fine needles, m.  $76.5-7^\circ$ , of which 0.55 part dissolves in 100 parts petrol. ether (d.  $0.64-0.66$ ) at  $16^\circ$ , and the  $\beta$ -form (B), monoclinic prisms, m.  $69-9.5^\circ$ , of which 5.14 parts dissolve in 100 parts petrol. ether. Upon further reduction with  $\text{H}$  and  $\text{Pt}$ , both forms give the same  $[\text{Me}_3\text{C}(\text{OH})\text{CH}_2]_n$ . Both forms yield a mixt. of *bromides*, a solid product, long, thin prisms, m.  $98.5-99^\circ$ , and a liquid product. A, however, yields considerably less of the solid bromide. In an attempt to det. the configuration of the 2 glycols, oxide formation was studied. Both A and B, heated with 15%  $\text{H}_2\text{SO}_4$  or warmed with  $\text{K}_2\text{SO}_4$  to  $140-60^\circ$ , gave the same  $\alpha$ -oxide, b.m.  $102-2.5^\circ$ , camphor-like odor,  $d_4^{20}$  0.8226,  $d_4^{17.5}$  0.8093,  $n_D^{17}$  1.40926. Study of the oxide formation by means of I indicated that the  $\alpha$ -form, reacted more readily than did the  $\beta$ -form and therefore probably possesses the maleonid configuration. Expts. on the hydrogenation showed that the quicker the addn. of the  $\text{H}$ , the greater the yield of the  $\alpha$ -isomer. C. J. WEST

**Syntheses utilizing organo-zinc derivatives; propylglyoxal.** E. E. BLAISE. Compt. rend. 175, 1216-8(1922).—Diketones cannot be directly prepd. by the action of the organo- $\text{Zn}$  derivs. on oxalyl chloride. They are formed by the condensation of the  $\text{Zn}$  compds. with the dichlorides of neutral oxalates of  $\text{HO}$  acids. Thus  $[\text{COCl}]_2$  by reaction with hydroxyisobutyric acid yields a diacid whose dichloride,  $[\text{Me}_3\text{C}(\text{COCl})\text{OC}(\text{O})]_n$ , con-

denses with  $\text{PrZnI}$ , yielding a mixt. of the *bishydroxyisobutyric cycloacetal of dibutylryl* (A) and the *bishydroxyisobutyric cycloacetal of propylglyoxal*,  $\text{Me}_2\text{C} \cdot \text{CO} \cdot \text{O} \cdot \text{C}(\text{C}_3\text{H}_7) \cdot$   $\text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{CMe}_2$  (B). A and B can be sepd. by refluxing the liquid mixt. with MeOH contg. 4% HCl, whereby A is unchanged, while B yields the *dimethyl acetal of propylglyoxal* (C). C is a colorless mobile liquid,  $b_{14}$  65–6°. It reduces  $\text{NH}_3 \cdot \text{AgNO}_3$ , but does not reduce Fehling soln. It gives a red color, turning to violet, with Schiff's reagent. A *disemicarbazone* is formed, insol. in EtOH, crystg. from 50% HOAc with 1 mol. HOAc in laminas, m. 250°. C forms an *osazone*, sol. in EtOH and  $\text{C}_6\text{H}_6$ , needles from HOAc, m. 105°. C on hydrolysis with 3%  $\text{H}_2\text{SO}_4$  yields *propylglyoxal* (D), a greenish brown liquid of strong odor,  $b_{16}$  36° [vapors also brown]. D cannot be preserved unchanged even in a sealed tube, polymerization apparently occurring; the presence of air causes immediate oxidation, with the production of butyric acid. The color change in aq. soln. indicates the formation of an unstable hydrate. D reduces  $\text{NH}_3 \cdot \text{AgNO}_3$  without addn. of alkali, and colors with Schiff's reagent. I. P. ROSE

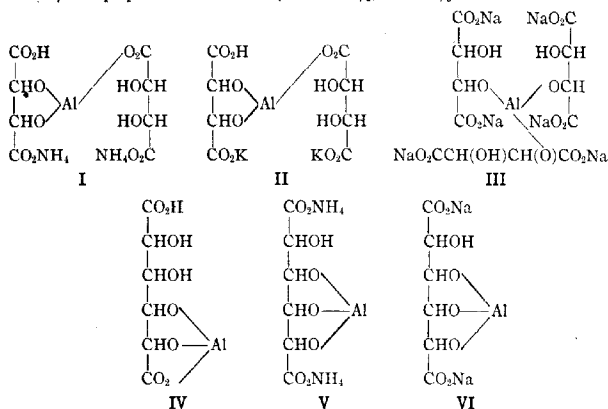
**Direct oxidation by oxygen or by air of the esters of alcohol-acids.** L. J. SIMON. *Compt. rend.* 175, 489–91 (1922).—Though several investigators have effected oxidation of  $\text{MeCH}(\text{OH})\text{CO}_2\text{H}$  (A) by  $\text{KMnO}_4$ , Br, etc., direct oxidation of a deriv. of A by O or air has not been accomplished. *Cold oxidation*.—The action of both air and O on  $\text{MeCH}(\text{OH})\text{CO}_2\text{Et}$  (B) is very slow, though accelerated by agitation and by light. Only after 1 week of agitation could  $\text{MeCOCO}_2\text{Et}$  (C) be detected. The independent reaction  $2\text{C} + \text{O}_2 \rightarrow 2\text{MeCHO} + 2\text{CO}_2 + 2\text{EtOH}$  also occurred under the influence of agitation and light. *Hot oxidation*.— $\text{MeCH}(\text{OH})\text{CO}_2\text{Me}$  (D), B,  $\text{MeCH}(\text{OH})\text{CO}_2\text{Bu}$  (E) and  $\text{MeCH}(\text{OH})\text{CO}_2\text{Am}$  were oxidized by a current of air when hot. With B and D, yields of 5–10% in 24–48 hrs., depending upon the air current, were obtained. Above certain temp. ranges, other products such as lactyllactates were formed, and mutual reactions among some of the products occurred. Oxidation of E for 20 hrs. at 180° gave a 9% yield of  $\text{MeCOCO}_2\text{Bu}$ . Oxidation under similar conditions of  $\text{CH}_2(\text{OH})\text{CO}_2\text{Et}$  gave  $\text{EtO}_2\text{CCHO}$ . These oxidations of A to pyruvate and to aldehyde +  $\text{CO}_2$  are considered to occur simultaneously in animal and vegetable metabolism.

C. C. DAVIS

**Complex aluminium salts of aliphatic hydroxy acids.** OSKAR GOLDMAN. *Biochem. Z.* 133, 459–68 (1922).—Complex Al salts, which may prove of pharmacol. interest, were prepd. from  $[\text{CH}(\text{OH})\text{CO}_2\text{H}]_3$ ,  $[\text{CH}(\text{OH})\text{CONH}_2]_3$ ,  $[\text{CH}(\text{OH})\text{CO}_2\text{NH}_4]_3$ ,  $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{K}$ ,  $[\text{CH}(\text{OH})\text{CO}_2\text{Na}]_3$ ,  $\text{HO}_2\text{C}[\text{CH}(\text{OH})]_2\text{CO}_2\text{H}$ ,  $\text{NH}_4\text{O}_2\text{C}[\text{CH}(\text{OH})]_2\text{CO}_2\text{NH}_4$ , and  $\text{NaO}_2\text{C}[\text{CH}(\text{OH})]_2\text{CO}_2\text{Na}$ . The salts in several instances were cryst., their aq. soln. was not pptd. by  $\text{NH}_4\text{OH}$  in the presence of  $\text{NH}_4\text{Cl}$  or on warming; nor did they ppt. protein solns. The conclusions of Hanuš and Quadrat, (cf. C. A. 4, 298) that mannitol, sucrose,  $\text{MeCH}(\text{OH})\text{CO}_2\text{Et}$ ,  $[\text{CH}(\text{OH})\text{CO}_2\text{Et}]_3$ ,  $\text{PhCH}(\text{OH})\text{CONH}_2$ ,  $\text{PhCH}(\text{OH})\text{CO}_2\text{Na}$  and  $\text{MeCH}(\text{OH})\text{CO}_2\text{NH}_4$  form no stable complex salts are verified. Apparently not only 2  $\text{CO}_2\text{H}$  groups, but also at least 4 OH groups, which may be drawn from more than 1 mol., are necessary for the formation of such a salt. The Al salt of tartaric amide is an apparent exception to this. Salts were prepd. by boiling an aq. soln. of the HO acid deriv. with excess of  $\text{Al}(\text{OH})_3$  freshly prepd. from 0.5 N  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{NH}_4\text{OH}$ . The soln. is filtered and coned. From  $[\text{CH}(\text{OH})\text{CONH}_2]_3$ , which is neutral in aq. soln., after heating with  $\text{Al}(\text{OH})_3$  and concn., an acid soln. is formed, from which a white solid crystallizes. Recrystd. from  $\text{H}_2\text{O}$ , its mol. wt. by titration was 178, C 24.09%, Al 13.11%. For  $\text{HO}_2\text{CCH} \cdot \text{O} \cdot \text{Al}(\text{OH})_2 \cdot \text{O} \cdot \text{CHCONH}_2$ , the mol. wt. is 158,

C 25.14%, Al 14.19%. An analogous Ca or Mg salt could not be prepd. From  $[\text{CH}(\text{OH})\text{CO}_2\text{H}]_3$  a gummy mass, amorphous and acid in soln., was obtained; its Al content

was 6.30%, corresponding to  $[\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2]_3\text{Al}$ . From  $[\text{CH}(\text{OH})\text{CO}_2\text{NH}_4]_3$  an amorphous powder, acid in soln., was prepd. Mol. wt. 394.5, Al 7.77%, N 8.95%. I requires mol. wt. 358, Al 7.56%, N 7.82%. From  $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{K}$  an amorphous material was prepd., mol. wt. 409.4, Al 5.29%, corresponding to II; from  $[\text{CH}(\text{OH})\text{CO}_2\text{Na}]_3$  a similar material, Al 4.00%, Na 22.15%, corresponding to formula III. Mucic acid was prepd. from lactose. It forms an Al salt easily sol. in  $\text{H}_2\text{O}$ , amorphous, having a mol. wt. 206, Al 10.84%; its structure is probably expressed by IV. No amide could be prepd. from mucic acid. A cryst. neutral  $\text{NH}_4$  salt was prepd. and this on treatment with  $\text{Al}(\text{OH})_3$  gave a cryst. salt. Recrystd. from  $\text{H}_2\text{O}$ , it m.  $231^\circ$  [decompn.]. This did not acetylate by Skraup's method. Analysis, C 25.53%, N 10.09%, Al 9.42%, indicated the constitution VI. A cryst. Na salt of similar constitution (VI) was prepd. from Na mucate, Na 16.90%, Al 9.62%.



I. P. ROLF

**Equilibrium between amino acids and formaldehyde in aqueous solution.** JULIUS SVEHLA. *Ber.* 56B, 331-7(1923).—In the case of glycocoll, alanine and valine, the equil. const. was detd. by means of the f.-p. lowering, while in the higher members of the series the relation between the soly. of the acids in  $\text{H}_2\text{O}$  and  $\text{HCHO}$  solns. of varying concn. was used. The values of  $K$  ( $C_{\text{HCHO}} \cdot C_{\text{Amino-acid}} / C_{\text{HCHO-acid}}$ ) follow: glycocoll, 1.73; alanine, 14.1; valine, 28.9; leucine, 36.8; aspartic acid, 25.7; glutamic acid, 30.7. No change was observed in the soly. of phenylalanine and tyrosine in  $\text{HCHO}$  of varying concn. Leucylglycine in dil. aq. soln. reacts with 2 mols.  $\text{HCHO}$ . C. J. WEST

**Chlorination of amino acid esters.** WILHELM TRAUBE AND HEINRICH GÖCKEL. *Ber.* 56B, 384-91(1923).—The action of  $\text{Cl}$  or  $\text{HOCl}$  upon  $\text{NH}_2$  acids in  $\text{H}_2\text{O}$  gives derivs. chlorinated in the  $\text{NH}_2$  group. Thus, passing  $\text{Cl}$  into  $\text{H}_2\text{NCO}_2\text{Et}$  in  $\text{H}_2\text{O}$  at room temp. gives *N*-chlorourethan (A),  $b_{30}$   $101-2^\circ$ , miscible with  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$ ,  $\text{CHCl}_3$ , slightly sol. in  $\text{H}_2\text{O}$ ; excess of  $\text{Cl}$  gives the  $\text{Cl}_2$ -deriv. A has a disagreeable odor and a harmful effect on the skin. Potassium salt (B), by salting out from 10%  $\text{KOH}$  with 50-60%  $\text{KOH}$  and then solid alkali, glistening prisms with  $2\text{H}_2\text{O}$ ; sodium salt, differs from the K salt by being hygroscopic. Silver salt, from the K salt and  $\text{AgNO}_3$ , powder. *N*-Chloro-*N*-methylurethan was prepd. by the action of  $\text{Cl}$  upon  $\text{MeHNCO}_2\text{Et}$  or by the action of  $\text{Me}_2\text{SO}_4$  upon an alk. soln. of A,  $b_{30}$   $57^\circ$ . The action of  $\text{ClCO}_2\text{Et}$  upon B gave principally  $\text{Cl}_2\text{NCO}_2\text{Et}$  and  $\text{NH}(\text{CO}_2\text{Et})_2$  in place of the expected  $\text{ClN}(\text{CO}_2\text{Et})_2$ . The action of



BzCl upon B gave a yellowish oil, probably the expected *N*-benzoyl-*N*-chlorourethan, since an excess of  $\text{H}_2\text{SO}_4$  transformed this into  $\text{BzNHCO}_2\text{Et}$ . It was impossible, through the action of Cl upon  $\text{NH}_2$  esters, to obtain mono-Cl derivs. Thus  $\text{H}_2\text{NCH}_2\text{CO}_2\text{Et}$  gave *N*-dichloroglycocol ester, oily. The *N*-dibromo derivative was obtained by the action of NaOBr as a reddish brown oil. These derivs. are not very stable and decomp. into the acid salt of the original ester. *N*-Dichloro- $\alpha$ -alanine ester, yellowish oil. The  $\text{Et}_2\text{O}$  soln. of A decomp. on standing for a short time, HCl being evolved and the cryst.  $\text{ClCH}_2\text{CH}(\text{NHCO}_2\text{Et})_2$  sepg. out.

C. J. WEST

**Methylisopyromucic acid and a method of differentiating between the acids of the sugar group.** L. J. SIMON AND A. J. A. GUILLAUMIN. *Compt. rend.* **175**, 1208-11 (1922).—*Methylisopyromucic acid*,  $\text{MeC}:\text{C}:\text{CH}:\text{C}(\text{OH})\text{CO}_2\text{O}$  (A), was prepd. in 8%

yield from rhamnonic lactone by distn. with  $\text{KHSO}_4$  (Chavanne, *Compt. rend.* **130**, 255), colorless crystals from HOAc, or by sublimation; A is volatile with steam, has a characteristic odor, m.  $133^\circ$ , is sol. in all org. solvents and  $\text{H}_2\text{O}$ . It cannot be titrated with phenolphthalein, but behaves as a phenol. In alk. soln. ( $\text{C}_2\text{H}_5\text{O}_2$ ) $_2\text{Pb}$  may be pptd. A reduces  $\text{Ag}_2\text{SO}_4$  and  $\text{AgCl}$ , without addn. of alkali. With Hg salts, a gelatinous ppt. is formed. It reduces acid or alk.  $\text{KMnO}_4$  in the cold. With BzCl it forms a *benzoyl derivative*, m.  $121^\circ$ . No ketone reactions have been observed, but it decolorizes  $\text{Br}_2$  and with  $\text{I}_2$  gives  $\text{CHI}_3$ . With  $\text{FeCl}_3$  A gives a more bluish coloration than the intense green which characterizes isopyromucic acid. The following technic has been developed by S. and G. to distinguish, according to the suggestion of Chavanne, between the acid derivs. of the pentoses and hexoses. 0.2 g. of acid, lactone, or ester, are heated in a test-tube, with 0.5 g. powdered  $\text{KHSO}_4$ ; to the condensed vapor is added  $\text{FeCl}_3$ . The appearance of a green color indicates the presence of a biacid deriv. of a hexose, or a monoacid deriv. of a pentose or methylpentose. Lack of color may indicate that the acid was a monoacid deriv. of a hexose, in which case a repetition of the test after careful oxidation of the acid will give a positive test.

I. P. ROSE

**Isomerism of  $\beta$ -benzylaminocrotonic ester, its ferric chloride reaction and that of related compounds.** ERICH BENARY. *Ber.* **56B**, 53-5 (1923).—Rugheimer (*C. A.* **10**, 1533) believed that Et  $\beta$ -benzylaminocrotonate (A) existed in a keto and an enol form, because of the different behavior of the 2 forms with  $\text{FeCl}_3$ . The color does not develop if NaOAc is used with the  $\text{FeCl}_3$ , which indicates that the color with  $\text{FeCl}_3$  alone is due to a hydrolysis into the base and  $\text{AcCH}_2\text{CO}_2\text{Et}$ . Other crotonic acid derivs. behave similarly. In  $\text{Et}_2\text{O}$  A gives a brown oily ppt. with  $\text{FeCl}_3$ , which is turned red by alc. In  $\text{AcMe}$   $\text{FeCl}_3$  gives a colorless ppt. Thus the supposition of a keto-enol tautomerism is not supported and it is also doubtful whether there exists a *cis-trans* isomerism.

C. J. WEST

**Commercial chlorination of organic compounds by means of free chlorine.** HENRI BARTHÉLÉMY. *Rev. prod. chim.* **25**, 685-94 (1922); *Chem. Trade J.* **71**, 603-4 (1922).—After describing the process of chlorination and precautions to be taken in general, B. describes chlorination without catalysts, photocatalytic chlorination (Sachs-Barthélémy process for the com. prepn. of chlorinated  $\text{CICO}_2\text{Me}$ ), and catalytic chlorination (using  $\text{Fe}$ ,  $\text{Fe}_2\text{Cl}_6$ ,  $\text{SbCl}_5$ ,  $\text{I}$ ,  $\text{S}$ ,  $\text{P}$ ,  $\text{PCl}_5$ ).

A. P.-C.

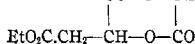
**Synthesis of muconic acid derivatives.** ERICH BENARY AND RUDOLF SCHINKOPF. *Ber.* **56B**, 354-62 (1923).—The reaction of  $\text{CH}_2\text{ClCH}(\text{OEt})\text{Cl}$  and  $\text{CHNa}(\text{CO}_2\text{Et})_2$  proceeds smoothly in ether, yielding tetraethyl 1,2-butene-1,1,4,4-tetracarboxylate (tetraethyl  $\Delta^{\alpha,\beta}$ -dihydromuconate- $\alpha,\beta$ -dicarboxylate) (A), b<sub>10</sub> 223-5°.  $\text{FeCl}_3$  in EtOH gives a bluish red color. Zn and AcOH reduce it to the butane deriv. Allowed to stand with satd. EtOH- $\text{NH}_3$  for several days, the monoethyl triamide results, needles from hot  $\text{H}_2\text{O}$ , decomp.  $230^\circ$ , while with aq.  $\text{NH}_4\text{OH}$  the tetraamide results as needles, decomp.  $257^\circ$ .

Sapond. with EtOH-KOH, the free acid is formed, amorphous, analyzed as the lead salt. If twice the amt. of  $\text{ClCH}_2\text{CH}(\text{OEt})\text{Cl}$  is used, the product of the above reaction is ethyl  $\alpha$ -carbethoxy- $\beta$ -ethoxy- $\alpha$ -chlorobutyrate, mobile oil,  $b_D^{20}$  149–52°. It gives no color with  $\text{FeCl}_3$ . Br in  $\text{CHCl}_3$  and A give tetraethyl  $\alpha,\beta,\gamma$ -tribromobutanetetra-carboxylate, 6-sided pyramids, m. 61–3°. Alc.  $\text{NH}_3$  gives an intense blue color. Warmed with  $\text{C}_6\text{H}_5\text{N}$  for 0.5 hr. at 100°, the bromide gives tetraethyl  $\alpha,\gamma$ -butadiene- $\alpha,\alpha,\delta,\delta$ -tetra-carboxylate, soft, felt-like needles, m. 56–7°. This ester also results by heating the bromide at 13 mm. to 120–50°. Boiled with 10 parts concd. HCl, the ester gives  $\beta,\gamma$ -diethoxybutane- $\alpha,\alpha,\delta,\delta$ -tetra-carboxylic acid, needles, m. 132° and evolve  $\text{CO}_2$  at 140°, and also  $\beta,\gamma$ -diethoxybutane- $\alpha,\delta$ -dicarboxylic acid, compact spears,  $b_D^{20}$  149°, m. 19.5°. The latter, treated with Br in  $\text{CHCl}_3$ , gave  $\alpha,\delta$ -dibromo- $\beta,\gamma$ -bis[ $\alpha'$ , $\beta'$ -dibromoethoxy]-butane- $\alpha,\delta$ -dicarboxylic acid, needles, m. 77–78°. C. J. WEST

The non-existence of crassulaceous malic acid. HARTWIG FRANZEN AND RUDOLPH OSTERTAG. Ber. 55B, 2995–3001(1922).—Textbooks refer to an optically active  $\text{HO}_2\text{CCH}(\text{OH})\text{CH}_2\text{CO}_2\text{H}$  (A), the properties of which differ in many ways from  $d$ - and  $l$ -A. A third optically active form of A should not be possible on stereochem. grounds. Werner is cited. The difference between ordinary A and crassulaceous A is based on the work of Meyer (Landw. vers. Stat. 21, 298(1878)), Schmidt (Arch. Pharm. 224, 535 (1886)) and Aberson (Ber. 31, 1432(1898)), and their grounds for believing in the difference in these 2 acids are that ordinary A and its  $\text{NH}_4$  and Ca salts are well crystd. whereas the salts of crassulaceous A and the acid itself do not cryst. well. The investigators evidently had impure material. From 28 kg. *Echeveria secunda glauca*, used as formerly, 23.7 l. of a light clear yellow juice were obtained. By pptn. with alc. a Ca salt was obtained which according to M. and S. should be the Ca salt of crassulaceous A. With dil. HCl the acid Ca salt was obtained. The Ca salt is not pure and is contaminated by  $\text{H}_2\text{PO}_4$ .  $\text{Hg}(\text{OAc})_2$  soln. gave a heavy white ppt. From the aq. soln. of the Ca salt ppt., using  $\text{H}_2\text{SO}_4$  and  $\text{Et}_2\text{O}$ , the free A was secured. After the  $\text{Et}_2\text{O}$  was distd. and the  $\text{H}_2\text{O}$  was evapd. at 60° a sirup was obtained which after standing several days over KOH and  $\text{H}_2\text{SO}_4$  did not crystallize. Ordinary A under the same conditions gave a cryst. mass. To show that the anhydride formation is not the cause of the anomalous behavior of crassulaceous A, mountain ash berry juice was treated in the same way and the A from this source gave crystals and not the sirup. Crassulaceous A was esterified and fractionated under 11–2 mm. The data show that the liquid obtained is a mixt. The fractions contain esters of acids other than A. The fractions were systematically converted into the hydrazides and in some case to the benzylidene derivs. of the hydrazides by a method previously used, (C. A. 16, 1795, 2350, 3199, 3499). The fraction b. 88–105° contained succinic ester. The fraction b. 105–25° consists largely of A ester; the yield of A dihydrazide was 94% of the computed amt. The fractions b. 125–8° and 128–30° were pure ester. In the case of the fraction b. 135–55° a pasty hydrazide sep'd. which pointed to the presence of citric acid ester. The fraction b. 155–65° when mixed with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  gave a clear mixt. at first, but it soon became cloudy and pasty. The fraction b. 176–8° gave A dihydrazide when shaken with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ . 1 g. ester gave 0.97 g. dihydrazide, colorless mass m. 178–9°. No cryst. structure could be detected when the product was magnified 300 diameters. When shaken with an aq. soln. of BzH benzylidene deriv. was obtained, m. 163–4°. It gave the Ag salt of A when sapond. and treated with  $\text{AgNO}_3$  and  $\text{HNO}_3$ . The ester b. 176–8° and cannot be the Et ester of A because the b. p. is too high. The sapon. no. of the ester shows that



it is malyimalic acid anhydride ester



The prod-

uct is present in *Echeveria*. The occurrence of this product is of biochem. interest.

When 2 mols. A give 1 mol. of malylnallic anhydride (B) 2  $\text{CO}_2\text{H}$  groups disappear; the plant is thus protected from the acidic action of A, alkalies being unnecessary. In case A be necessary for the life of the plant, a fermentative splitting of the anhydride is indicated. The presence of B caused the mixt. of acids from *Echeveria* to remain noncryst. When A anhydride is added to A and the mixt. is evapd. in a vacuum in the manner employed in the case of the plant juice a clear noncryst. mass is obtained with properties resembling crassulaceous A. Crassulaceous A is really ordinary malic acid.

H. F. WILLIAMS

The pyrimidines contained in tuberculinic acid, the nucleic acid of tubercle bacilli. T. B. JOHNSON AND E. B. BROWN. *J. Biol. Chem.* **54**, 731-7(1922); cf. *C. A.* **17**, 1261.—Tuberculinic acid was hydrolyzed with  $\text{H}_2\text{SO}_4$  and examd. for pyrimidines. From 7 g. there were obtained 0.1035 g. cytosine and 0.0756 g. thymine. No color reactions for uracil could be obtained.

I. GREENWALD

Preparation of potassium hydroxylamine-isodisulfonate. F. RASCHIG. *Ber.* **56B**, 206-8(1923).—150 g.  $\text{NaNO}_2$  are mixed with 1000 g. ice and 1200 cc. 5 N  $\text{NaHSO}_3$  run in with stirring, the temp. being kept below  $5^\circ$ . The ice, if any is present, is removed, the soln. transferred to a 3-l. flask and treated with 600 g.  $\text{PbO}_2$  with continuous shaking; the mixt. is then heated on the  $\text{H}_2\text{O}$  bath for 25 min., with shaking every min., and finally 800 g. tech. KCl are added and the warming is continued until soln. results. The  $\text{PbCl}_2$  is filtered off while hot and the K salt allowed to crystallize for 3 days at  $0^\circ$ . Yield, 790 g. of  $(\text{KSO}_3\text{O})_2\text{N}(\text{SO}_3\text{K})_2\text{H}_2\text{O}$ . One of the  $\text{SO}_3\text{K}$  groups is split off by adding 423 g. finely pulverized salt to 800 cc. boiling  $\text{H}_2\text{O}$  contg. 1 cc. dil. HCl. Upon cooling 90% of the theory of  $\text{SO}_3\text{K.O.NH.SO}_3\text{K}$  seps.

C. J. WEST

Action of uranyl acetate on organic compounds. I. The action of uranyl acetate on tartaric acid and its salts. FRITZ KOPATSCHEK. *Anales asoc. quim. Argentina* **10**, 133-51(1922).—Uranyl acetate has no effect upon the optical rotation of carbohydrates in soln. With other compds. contg. one or more central OH groups optically active compds. are formed, which K. proposes to call "aceturanilic compds." These are unstable and are sensitive to light. The reaction with tartaric acid was studied in detail. It is influenced by concn. The optical rotation is greatly increased, but the amt. of increase is affected more or less by the addn. of almost any common inorg. salt;  $\text{Na}_2\text{CO}_3$  nullifies it almost completely.

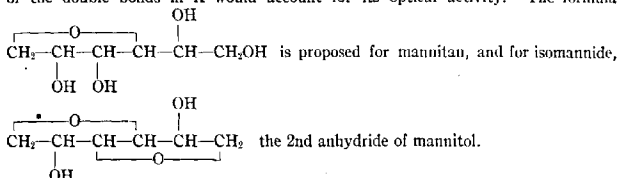
L. E. GILSON

Preparation of ethanetetra-carboxylic acid. C. MANNICH AND E. GANZ. *Ber.* **55B**, 3509-10(1922).—The method of prepn. of Buchner and Witter (*Ber.* **25**, 1158(1892)), who sapond. the corresponding ester with NaOH, was found to be unsatisfactory in amts. larger than 3 g. Acid sapon. was also unsatisfactory; concd. HCl does not act on the ester, while  $\text{H}_2\text{SO}_4$  is too difficult to sep. from the tetra- $\text{CO}_2\text{H}$  acid. A method for the prepn. of relatively large quantities was found to consist in the reduction of  $(\text{HO}_2\text{C})_2\text{C}:\text{C}(\text{CO}_2\text{H})_2$  (A) with Pd and H. A is readily prepd. and is usually more stable than the satd. acid. The reduction goes fairly well, though some  $\text{CO}_2$  is split off. 14 g. of A in 40 cc. acetone is reduced with charcoal impregnated with Pd and shaken with H until absorption ends. At least 100 cc. H should be absorbed in 0.5 hr. 1260 cc. H in all is absorbed. The filtered soln. is concd. and the product recrystd. from acetone. It m.  $167-9^\circ$  (decompn.).

E. H. VOLWILER

Cyclic derivatives of mannitol. P. VAN ROMBURGH AND J. H. N. VAN DER BURG. *Proc. Acad. Sci. Amsterdam* **25**, 335-40(1922).—The oxide  $\text{C}_6\text{H}_8\text{O}$  (A) obtained by heating mannitol hexaformate adds Br to form a dibromide,  $\text{C}_6\text{H}_8\text{Br}_2\text{O}$ , b<sub>15</sub>  $118.5^\circ$ . Reduction of A with H at 2 atm. in the presence of colloidal Pd gives a satd. oxide  $\text{C}_6\text{H}_{12}\text{O}$  (B), b.  $103-6^\circ$ . Assuming that A is  $\alpha$ -vinylidihydrofuran, B would be  $\gamma$ -hexylene oxide, whereas the formula proposed by Windaus and Tomich should give on reduction  $\delta$ -hexylene oxide. Attempts to prep. a cryst. benzoate from the glycol corresponding to

**B** were unsuccessful. However, the piperidinium derivs. of the dibromides from both  $\gamma$ - and  $\delta$ -hexylene glycols were easily prepd.  $\alpha$ -Methylpentamethylenepiperidinium bromide,  $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CHMe} \end{array} \text{NBr}-\text{CH}_2-\text{CH}_2-\text{CH}_2$ , prepd. from 1,5-dibromohexane and excess of piperidine, white crystals from EtOH-Et<sub>2</sub>O, m. 290°.  $\alpha$ -Ethyl homolog, prepd. from 1,4-dibromohexane and piperidine, m. 270°. **B** when converted into the bromide and treated in the same way gave a cryst. substance m. 269°, and a mixt. of this with the preceding m. sharply 269°. The identity of **B** was further established by comparing the m. ps. of the PtCl<sub>4</sub> double salts of the piperidinium bromides. **A** is therefore  $\alpha$ -vinylidihydrofuran, and **B** is  $\alpha$ -ethyltetrahydrofuran. No other arrangement of the double bonds in **A** would account for its optical activity. The formula



A. W. DOX

**The action of ammonia and amino compounds on reducing sugars. I. The action of ammonia on dextrose and levulose.** A. R. LING AND D. R. NANJL. *J. Soc. Chem. Ind.* **41**, 151-5T(1923).—This investigation was undertaken to explain the reactions involved in the manuf. of caramel by the NH<sub>3</sub> process. In this method NH<sub>3</sub> and dextrose are allowed to react at 35-40° and the compd. thus formed is heated to about 100° when a vigorous exothermic reaction takes place and dark colored substances are produced. Heating at 35° for 1.5-2 hrs. a mixt. of a 20% dextrose soln. and slightly more than the mol. proportion of NH<sub>3</sub>, and evapn. of the product under diminished pressure at 37-8° give *glucose-ammonia*, a pale amber-colored friable mass,  $[\alpha]_D^{15.6}$  4.4°. It is very hygroscopic, and in the solid state gives off NH<sub>3</sub>, reduces Fehling soln. and NH<sub>3</sub>-AgNO<sub>3</sub> and behaves as an aldehyde. The NH<sub>3</sub> combines with the aldehyde-hydrate (with the elimination of H<sub>2</sub>O) which is present in the soln. in equil. with  $\alpha$ -glucose and  $\beta$ -glucose. As the aldehyde-hydrate is removed from the soln. as glucose-NH<sub>3</sub> the equil. thus disturbed is restored by the conversion of more glucose into the hydrate, so that in the presence of an excess of NH<sub>3</sub> the dextrose is completely converted into the NH<sub>3</sub> compd. By bubbling air through a soln. of glucose-NH<sub>3</sub> for several weeks, evapg. over H<sub>2</sub>SO<sub>4</sub> in a vacuum desiccator and extg. with abs. EtOH and Et<sub>2</sub>O a sirup is obtained, with  $[\alpha]_D$  4.4°, and with a reducing power towards Fehling soln. higher than that of dextrose (100:88). The rotation of this sugar being the same as glucose-NH<sub>3</sub> indicates that in the concns. worked with (20 g. per 100 cc.) the glucose-NH<sub>3</sub> is entirely dissociated. The sugar obtained from glucose-NH<sub>3</sub> reduces KMnO<sub>4</sub> in dil. soln. at ordinary temp., a property of  $\gamma$ -glucose. It consists of a mixt. of aldose and ketose in equil. The equil. is changed according to the reaction of the soln. In 0.25 N HCl 100% aldose is present. The interaction of levulose and NH<sub>3</sub>, under conditions like those for glucose, gives aldose-NH<sub>3</sub>, the soln. of which behaves in every way similarly to that from dextrose. The removal of NH<sub>3</sub> from this soln. gives a mixt. in equil. of aldoses and ketoses. The relative amts. of aldose and ketose in these sugars was found by the iodometric detn. of the aldose.

G. W. STRATTON

**Tetralevoglucosan and tetraglucosan.** HANS PRINGSHEIM AND KARL SCHMALZ. *Ber.* **55B**, 3001-7(1922).—The anhydro sugars, the polyamyloses, obtained from starch and glycogen by fermentation with *Bacillus mucerans* have 2 characteristic properties.

When acetylated with  $\text{Ac}_2\text{O}$  and  $\text{ZnCl}_2$  they are depolymerized to the Ac deriv. of the fundamental compd. (C. A. 7, 345) and by methylation even under the most energetic action only 2 Me groups are introduced into every glucose radical. One HO group remains free (C. A. 16, 1745, 3875). Tetralevoglucosan (A) and tetraglucosan (B) were studied to ascertain whether both these properties are characteristic for any other polymerization products of anhydro sugars. By heating these products with  $\text{Ac}_2\text{O}$  and anhyd.  $\text{NaOAc}$ , Pictet prepd. an octaacetate and this compd. contained one OH group which was not attacked. A was prepd. according to the method of Pictet, with minor modifications. 100 g. starch were distd. in a 2-l. Jena distg. flask at 200–300° under reduced pressure during 1–1.5 hrs. The sirup was taken up in abs. alc., filtered and allowed to cryst. in an ice-salt mixt. The brown cryst. powder, levoglucosan (C), was crystd. from alc., and was then colored slightly brown, and after treatment with bone black 16 g. pure product was obtained. 10 g. C with 0.1–0.2 g.  $\text{ZnCl}_2$  in an oil bath were heated to 160°. The sugar melted and polymerization started from those parts of the melt which came in contact with the  $\text{ZnCl}_2$ . The whole mass soon became solid. The heating was continued for 1–2 hrs. The reaction product was dissolved in a little  $\text{H}_2\text{O}$  and most of the impurities were pptd. with an equal vol. of abs. alc. and the soln. treated with bone black in 300–400 cc. abs. alc. and filtered. Warm solns. were not used since it was feared that the HCl from the hydrolyzed  $\text{ZnCl}_2$  would decomp. the polysaccharides. A was obtained as a granular, white, amorphous mass which was easily filtered. The product first obtained showed reducing properties but when pptd. from the aq. soln. with alc. the reducing properties disappeared, and the rotation increased, yet the value never reached that given by Pictet, *vis.*, + 100°. 8.5 g. of material of 85° rotation were obtained. 2 g. A in 20 cc.  $\text{Ac}_2\text{O}$  and a piece of  $\text{ZnCl}_2$  the size of a pea were warmed on the water bath. After a few min. there action set in with foaming and then the light brown soln. was poured into  $\text{H}_2\text{O}$ . When the oil product solidified, it was filtered, and dried *in vacuo*. Dodecaacetyltetralevoglucosan is easily sol. in all org. solvents except  $\text{Et}_2\text{O}$  and petr. ether, and shows no tendency to crystallize. It is pptd. from its  $\text{C}_6\text{H}_5$  soln. by petr. ether and is hygroscopic. It softens at 108–9° and at 125° is clear,  $[\alpha]_D^{20}$  68.37° in HOAc. 4 g. A in 5 cc.  $\text{H}_2\text{O}$  were treated with 2.2 g. NaOH, making a 30% soln. In the course of 4 hrs. 23.3 g.  $\text{Me}_2\text{SO}$  and 49.4 g. 30% NaOH were added at 70°; the mixt. was stirred in a turbine. The soln. was neutralized with HOAc and the product was then taken up in  $\text{CHCl}_3$ , dried with  $\text{CaCl}_2$  and then the soln. was evapd. A yellow sirup remained. This did not reduce Fehling soln. Its compn. corresponds to  $[\text{C}_6\text{H}_7\text{O}_5(\text{OMe})_4]_n$ . Dodecamethyltetralevoglucosan (D). This product was methylated and the completely methylated product showed no reaction toward Fehling soln. and was sol. in all solvents except petr. ether. 4 g. D were refluxed with 50 cc. 5%  $\text{H}_2\text{SO}_4$  for 1 hr. The  $\text{H}_2\text{SO}_4$  was removed as  $\text{BaSO}_4$  (quant.) and a sirupy residue remained, which was refluxed 4 hrs. with equal parts  $\text{PhNH}_2$  and abs. alc. After cooling, long needles, tetramethylglucose anilide, m. 136–7°, sepd. from abs. alc. The  $\text{PhNH}_2$  was removed from the filtrate and the residue from the evapd. filtrate showed no tendency to crystallize. The aniline was split off by boiling the compd. with 20 cc. 5%  $\text{H}_2\text{SO}_4$ . The acid was removed as  $\text{BaSO}_4$ , and the sirup remaining gave dimethylglucose. It gave no osazone. The polymerization of glucose was effected as Pictet described it; the yield never amounted to over 10% because of oxidation and decompn. products. B reduced Fehling soln. when the mixt. was heated but no osazone formation was observed. Dodecaacetyltetraglucosan was prepd., hygroscopic compd.,  $[\alpha]_D^{20}$  70.82° in HOAc. Dodecamethyltetraglucosan was also prepd. Octaacetyltetraglucosan (Pictet) was prepd. by heating tetraglucosan with  $\text{Ac}_2\text{O}$  and anhyd. NaOAc. Data on the Ac content and the mol. wt. were secured. H. E. WILLIAMS

Acetyl derivatives of xylan. EML. HEUSER AND PAUL. SCHLOSSER. Ber. 56B, 392–5(1923).—H. and Ruppel (C. A. 17, 390) have shown, by the action of MeI upon

xylan, that this contains 2 replaceable H atoms. This work is confirmed by the action of  $\text{Ac}_2\text{O}$ , which reacts upon xylan at the boiling temp., or in the presence of  $\text{C}_4\text{H}_9\text{N}$  at  $70^\circ$  or of  $\text{HNO}_3$  at  $60^\circ$ , and of  $\text{AcCl}$  at  $50^\circ$ , the resulting product in each case being a *diacetylxylan*, amorphous, very slightly hygroscopic powder, easily sol. in  $\text{C}_4\text{H}_9\text{N}$ , difficultly sol. in  $\text{CHCl}_3$  and  $\text{AcMe}$ , insol. in  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ ,  $\text{MeOH}$  and  $\text{Et}_2\text{O}$ . In order to render the xylan reactive, it is allowed to stand in distd.  $\text{H}_2\text{O}$  for 48 hrs., and the excess  $\text{H}_2\text{O}$  washed out with  $\text{AcOH}$ .

C. J. WEST

**Remarks upon the work:** "Cellulose-copper compounds" by Kurt Hess and Ernst Messmer. WILHELM TRAUBE. *Ber.* 56B, 268-74(1923).—Polemical. Cf. H. and M., C. A. 17, 208, and T., C. A. 16, 1934.

C. J. WEST

"Aromatic" carbon. K. v. AUWERS. *Ber.* 56B, 69-76(1923).—Polemical against v. Steiger, C. A. 17, 380.

C. J. WEST

The action of sodammonium on aniline and its homologs. M. PRON. *Compt. rend.* 175, 1213-6(1922).—*Monosodium anilide*,  $\text{PhNHNa}$ , and its homologs, were prepd. by allowing the reaction between 1 or 2 atoms of Na, 1 mol. of  $\text{PhNH}_2$ , and excess liquid  $\text{NH}_3$  to proceed in an autoclave at room temp. The Na is completely substituted after 7 days. After evapn. of the  $\text{NH}_3$  the ether-sol. material is extd. from the insol.  $\text{NaNH}_2$ , and after concn. a glassy light yellow solid remains, which titrates for  $\text{PhNHNa}$ . With  $\text{H}_2\text{O}$ , a violent decompn. occurs, yielding  $\text{PhNH}_2$ . With  $\text{EtI}$ ,  $\text{PhNHEt}$  is formed by violent decompn. even at  $-40^\circ$ . The di-Na deriv. could not be prepd. by this method. From  $\text{PhNHEt}$ , *monosodium ethylanilide* is obtained, a white solid, reacting violently with  $\text{H}_2\text{O}$  and  $\text{EtI}$ . From *o*-toluidine the corresponding *monosodium derivative* is formed after 15 days. It is a yellowish white solid, reacting more gently with  $\text{EtI}$  in  $\text{Et}_2\text{O}$  than the lower homologs. From  $\text{Ph}_2\text{NH}$ , *monosodium diphenylamide* is formed, a white solid, relatively insol. in  $\text{Et}_2\text{O}$ . From  $\text{PhCH}_2\text{NH}_2$ , the Na deriv. could not be prepd.

I. P. ROLF

**Molecular weight determinations in the arsonic acid series.** RICHARD LORENZ AND ELISABETH BREHMER. *Ber.* 56B, 174-6(1923).—The mol. wts. were detd. by the b.-p. method in  $\text{H}_2\text{O}$ . The degree of dissociation  $\gamma$  was calcd. from the formula  $-\frac{Kv}{\gamma} + \sqrt{Kv}$ ,  $v$  being the no. of l. contg. 1 mol. in soln. and  $K$  the dissociation const. from cond. data. The mol. wts. indicated the simple form with the exception of *o*-phenylenediaminearsonic acid, which has twice the simple mol. wt. The following values of  $\gamma$  are reported: arsanilic acid, 0.0103; *o*-toluidinarsonic acid, 0.0101; resorcinolarsonic acid, 0.025; 3-nitro-4-aminophenylarsonic acid, 0.060; 4-hydroxy deriv., 0.0399; 3-nitrophenylarsonic acid, 0.051; *p*-phenylenediarsonic acid, 0.097.

C. J. WEST

**Aromatic sulfonic acids.** E. KNÖVENAGEL AND A. RÖMER. *Ber.* 56B, 215-7 (1923).—The action of 1 mol. or less of  $\text{PCl}_5$  upon  $\text{PhSO}_2\text{Na}$  gives  $\text{PhSO}_2\text{SPh}$ , m.  $45^\circ$ , while an excess  $\text{PCl}_5$  reduces this ester to  $\text{Ph}_2\text{S}$ , m.  $60^\circ$ , the yield in both cases being about 90%. The  $\text{Fe}^3$  salt in  $\text{C}_6\text{H}_4$  is also changed to the ester by  $\text{PCl}_5$ .  $\text{SOCl}_2$  and  $\text{PhSO}_2\text{Na}$  in  $\text{Et}_2\text{O}$  give  $\text{PhSO}_2\text{Cl}$  as well as the ester. In the case of  $\text{SO}_2\text{Cl}_2$  only the chloride is observed. The action of  $\text{PhNH}_2$  upon  $\text{PhSO}_2\text{H}$  in  $\text{Et}_2\text{O}$ , followed by soln. in  $\text{EtOH}$  and pptn. by  $\text{Et}_2\text{O}$ , gave  $\text{PhNH}_2\text{SO}_2\text{Ph}$ . The action of benzaniline, benzoin anil, acetophenone anil and dypnonanil upon  $\text{PhSO}_2\text{H}$  gave addn. products which were easily transformed into  $\text{PhNH}_2\text{SO}_2\text{Ph}$ . Acetone anil gave a yellowish green product, m.  $112^\circ$ . This is not decompd. by  $\text{Na}_2\text{CO}_3$ . The action of  $\text{PhNMeCMe:CH}_2$  upon  $\text{PhSO}_2\text{H}$  gives a yellowish green product, m.  $92^\circ$  ( $\text{Et}_2\text{O}$ -sol.) and an  $\text{Et}_2\text{O}$ -insol. compd. m.  $105^\circ$ . Qual. soly. of the salts of  $\text{PhSO}_2\text{H}$  is given.

C. J. WEST

**Several bromine derivatives of thymol.** HANS JOST AND FRIEDRICH RICHTER. *Ber.* 56B, 119-23(1923); cf. Dannenberg, *Monatsh.* 24, 67.—The action of 0.4 atom Br upon 0.1 mol. thymol. in  $\text{AcOH}$  at  $0^\circ$  gives *2,4-dibromothymol* (A), long transparent prisms, m.  $3.5-4^\circ$ ,  $b_{14}$   $160-1^\circ$ ,  $b_{16}$   $175^\circ$ ,  $d_{13}^{25}$  1.6631,  $d_{17.4}^{25}$  1.6588. The *benzoate* forms

needles, m. 89–90° (D. gives 80–81°). The action of an excess of Br at room temp., of NaOBr or Ca(OBr)<sub>2</sub> upon thymol gives a ketobromide (*tribromo-p-menthadienone*), large, deep yellow plates, m. 59–60°, decomp. 130°. It is insol. in alkali and liberates 2 atoms of I from KI. Reduction of the ketobromide with SnCl<sub>2</sub> gave A. Conc'd. H<sub>2</sub>SO<sub>4</sub> gives *2,4,6-tribromo-m-cresol*, silk-like needles, m. 76–9°. Shaken with 4% KOH in CCl<sub>4</sub>, an amorphous brown product is obtained, which decomp. 220–30° and may be dibromodithymol. Owing to its colloidal nature in solvents such as C<sub>6</sub>H<sub>6</sub>, it was not further investigated.

C. J. Wess

**Simplified preparation of several organic compounds. I. Nitrophenetoles and nitroanisole.** H. VAN ERP. *Ber.* 56B, 217–21 (1923).—The new method consists in heating the K salt of the nitrophenol with KFeSO<sub>4</sub> in the presence of C<sub>2</sub>H<sub>5</sub>(OH)<sub>2</sub> at 180–200°; this permits the use of an open vessel. The yield of 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OEt was 86%; of 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OEt, 90%; this b<sub>8</sub> 134.2°, b<sub>9</sub> 136°, b<sub>10</sub> 138.4, b<sub>12</sub> 142.8°, b<sub>16</sub> 149.3°; n<sub>D</sub> at 15°, 1.5451; at 20°, 1.5425; at 25°, 1.5400; at 30°, 1.5375; d<sub>15</sub> 1.1903. The yield of 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(OEt) was only 56%, while the 6-Cl deriv. could not be prep'd. this way. 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OMe was obtained in 87% yields.

C. J. Wess

**Beckmann rearrangement in o- and p-quinone oximes.** ERNST BECKMANN AND OTTO LIESCHE. *Ber.* 56B, 1–23 (1923).—Because of the growing importance of the Beckmann rearrangement for the detn. of the constitution of org. compds., it is desirable to know the behavior of o- and p-quinone oximes. The rearrangement of β-naphthoquinone oxime, whether by means of AcOH-Ac<sub>2</sub>O-HCl, PhSO<sub>3</sub>Cl in C<sub>6</sub>H<sub>5</sub>N or by the action of PCl<sub>5</sub>, gives in each case the substance C<sub>10</sub>H<sub>7</sub>O<sub>2</sub>N, m. 179°; this is a monobasic acid, of which the Ag, Na, K and Ba salts were prep'd. Sapon. with NaOH, it yields cinnamic-o-carboxylic acid (*Ber.* 10, 2203). The action of NH<sub>3</sub> upon the intermediate chloride gives a compound C<sub>10</sub>H<sub>8</sub>ON<sub>2</sub>, m. 207°. Under the above conditions of rearrangement the dioxime yields an anhydride (*Ber.* 17, 215). Ac<sub>2</sub>O and HCl in AcOH, reacting with the α-monoxime, gave a compound, C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>NCl<sub>2</sub>, contg. an Ac group, m. 163°. PhSO<sub>3</sub>Cl in C<sub>6</sub>H<sub>5</sub>N gave a benzenesulfonic ester, felt-like needles, m. 183–4°. AcCl gave no definite product, while Ac<sub>2</sub>O and AcOH gave an acetate, brown, glistening needles, m. 132.5°. The α-dioxime gave a N-diacetate (*Ber.* 21, 428). p-HOC<sub>6</sub>H<sub>4</sub>NO and PhSO<sub>3</sub>Cl, allowed to stand 12 hrs. and then warmed 20 min., gave the compound CH:CH.O:CH:CH.CO.NH, yellowish brown needles, m. 224°. The alk. soln. gives

a series of characteristic ppts. with metallic salts. Benzoate, leaflets, m. 189–90°. p-C<sub>6</sub>H<sub>4</sub>(NOH)<sub>2</sub> and PhSO<sub>3</sub>Cl gave only the corresponding ester, m. 175–8°. The other agents gave Cl-contg. products or smears. The rearrangement product of anthraquinone monoxime (*Ber.* 27, 2125) yields 2'-aminodiphenyl ketone-2-carboxylic acid upon soln. in alkali and pptn. with acid, m. 199° with formation of the rearrangement product. Silver salt, fine needles. Methyl ester, m. 168–73°; this was diazotized and coupled with Me<sub>2</sub>NPh, giving a green dye with metallic luster and easily sublimed. Anthraquinone oxime phosphate by the action of H<sub>2</sub>O upon the reaction product of the oxime, POCl<sub>3</sub> and PCl<sub>5</sub>, analyzed as the silver salt. Benzenesulfonic ester, fine needles, m. 154°. The rearrangement product gave an oxime, C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>, rectangular plates from EtOH, needles from AcOH, decomp. 243°. Benzoate, m. 209°. Rearrangement of the new oxime gave Anderlini's phthalyl-o-phenylenediamine (*Gazz. chim. ital.* 24, I, 145), which is unstable and gives 2-phenylbenzimidazole-2'-carboxylic acid.

C. J. Wess

**The action of iodine upon alkaline phenol solutions.** G. VORTMANN. *Ber.* 56B, 234–46 (1923).—Thirty years ago Messinger and V. described the action of I upon alk. PhOH solns. and the prep'n. of diiodophenol iodide. Lately this work has been questioned, and the comp'd. in question has been stated to be a mixt. of Lautemann's red, (A) and I<sub>2</sub>C<sub>6</sub>H<sub>2</sub>OH. According to V. the action of I upon PhOH depends upon the amt.

of alkali present, 1, 2, or 3 I entering the PhOH mol. according to whether 1, 2, or 3 mols. NaOH are present. In the presence of an excess of alkali,  $I_3C_6H_5OH$  is 1st transformed into the tautomeric diiodophenol iodide and then gradually into A. The iodide may be isolated by extg. with AcMe, in which the final product is practically insol. It forms dark violet-brown crystals, sol. in  $CHCl_3$  and  $C_6H_6$  with a red color, and m.  $122^\circ$ . Characteristic of the iodide is the violet color produced upon addn. of  $Na_2S_2O_3$  to a dil. AcMe soln. The transformation of  $I_3C_6H_5OH$  into A is accelerated by the addn. of oxidizing agents, such as NaOCl,  $H_2O_2$ ,  $KIO_3$ , etc. The compd.  $C_6H_5I_2(O):I_2$  is assumed as an intermediate step. The reduction of A with AcOH and  $SnCl_2 \cdot HCl$  leads to the formation of a colorless compd., showing the same soly. as A. This has been obtained by Hunter and Woollett (C. A. 15, 680); they considered it an isomeric product, but V. prefers to view it as a hydrated product with 4 additional H. Ten % NaOH also changes A, giving an amorphous, leather-colored insol. product, which is being investigated.

C. J. WEST

**N-Carboxylic acid anhydrides.** FRIEDRICH FUCHS. *Ber.* 55B, 2943(1922).—Curtius and Sieber (C. A. 16, 3882) stated that N-carboxylic anhydrides were prepd. by Leuchs by the action of  $SOCl_2$  on N-carbomethoxy-C-phenylaminoacetic acid and F. states that the same compd. was prepd. in a better manner by the action of  $COCl_2$  on amino acids. Into a cooled alk. aq. soln. of  $PhNHCH_2CO_2H$  (A)  $COCl_2$  is passed and fine needles of  $PhNHCH_2CO_2O.CO$  (B) sep. The investigation was undertaken in

order to recover the last traces of  $PhNHCH_2CO_2H$  from the alk. mother liquors. B with  $PhNH_2$  gave the anilide and with alc. the ester of A. The N-carboxylic acid anhydride prepd. from  $MeC_6H_4NHCH_2CO_2H$  by the action of  $COCl_2$  is more stable and better suited for further work than is B.

H. E. WILLIAMS

**Constitution of dianhydrodi[acetylanthranilic acid].** GUSTAV HELLER and HERBERT GRUNDMANN. *Ber.* 56B, 200-5(1923).—This compd. was obtained by Anschütz and Schmidt by the action of  $POCl_3$  upon acetylanthranilic acid (*Ber.* 35, 3463). It was also obtained as follows: *o*- $H_2NC_6H_4CO_2SO_2C_6H_4Me$ , boiled with  $Ac_2O$  for 0.5 hr., gave the mixed anhydride of  $\alpha$ -methyl- $\gamma$ -hydroxyquinoline- $\beta$ -[carboxylic acid-*o*-carboxyanilide] and toluene-*p*-sulfonic acid,  $C_{22}H_{20}O_4N_2S_2$ , pale yellow, m.  $214-5^\circ$  (decompn.). Upon soln. in alkali and acidification,  $\alpha$ -methyl- $\gamma$ -hydroxyquinoline- $\beta$ -[carboxylic acid-*o*-carboxyanilide], m.  $249-50^\circ$ , sepd.; this is identical with A. and S.'s compd. Heated in a sealed tube with 3 parts AcOH and 2 parts concd. HCl 4 hrs. at  $130-40^\circ$ , a 93% yield of  $\gamma$ -hydroxyquinoline was obtained. [Benzoylsulfonylanthranilic acid]-acetic acid anhydride, fine needles, m.  $212^\circ$ . Anthranilic acid-*p*-toluenesulfonate, by heating *o*- $H_2NC_6H_4CO_2SO_2C_6H_4Me$  with 2 parts AcOH and 1 part HCl at  $140^\circ$ , fine needles, m.  $218^\circ$  (decompn.).

C. J. WEST

**Esters of anisic acid.** L. G. RADCLIFFE and W. H. BRINDLEY. *Perfumery Essent. Oil Record* 13, 414-5(1922).—The present research resulted in the prepn. of a no. of new esters, but only in the case of the lower members of the aliphatic series did they possess pronounced odors, the higher members being practically odorless. Phys. consts. were detd. as follows: Me ester, m.  $48^\circ$ , b.  $256^\circ$ ; Et ester,  $d_4^{16.5}$  1.106, m.  $7-8^\circ$ , b.  $263^\circ$ ,  $n_{18.5}$  1.5245; propyl ester,  $d_4^{16.5}$  1.09,  $b_{46}$   $176^\circ$ ,  $n_{18.5}$  1.5149; butyl ester,  $d_4^{16.5}$  1.054,  $b_{46}$   $183^\circ$ ,  $n_{18.5}$  1.5141; isobutyl ester,  $d_4^{16.5}$  1.052,  $b_{46}$   $170^\circ$ ,  $n_{18.5}$  1.5072; isomyl ester,  $d_4^{16.5}$  1.040,  $b_{20}$   $188^\circ$ ,  $n_{18.5}$  1.5091; phenyl propyl ester,  $d_4^{16.5}$  1.111,  $b_{26}$   $256^\circ$ ,  $n_{18.5}$  1.5623.

W. O. E.

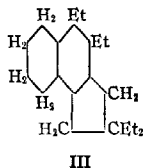
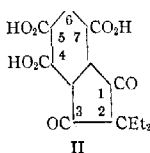
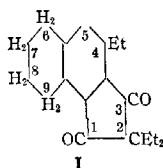
**Acidity of gallaldehyde.** M. NIERENSTEIN. *Ber.* 55B, 3581(1922).—Rosenmund and Zetzsche (C. A. 12, 2569), because of the apparent high acidity of gallaldehyde, criticized the theory of N. (C. A. 3, 2129) concerning its formation from gallotannin by hydrolysis. Since then, however, R. and Pfannkuch (C. A. 17, 743); have shown the incorrectness of this argument, which nullifies the original criticism. E. H. VOLWILER



Gallic aldehyde of M. Nierenstein. K. W. ROSENMUND. *Ber.* 56B, 136(1923).—Polemical. Cf. preceding abstr. C. J. Wzsr

Chinese tannin. J. HERZIG. *Ber.* 56B, 221-8(1923); cf. Herzig and Tscherne, *Ber.* 38, 989.—In the methylation of tannin with  $\text{CH}_3\text{N}_3$  better results are obtained by using an  $\text{Et}_2\text{O}$  soln. which has been fractionally distd. The use of the ordinary prepn. appears to cause a partial hydrolysis of the tannin with the formation of a product of higher MeO content (over 40% as compared with 38.05 for a normal methylotannin). Methylation of Freudenberg's Chinese tannin (*C. A.* 17, 1002) gave about 70% methylotannin with 38.09% MeO and  $[\alpha]_D^{25}$  of 12.44°. In 1 expt. it was observed that a part of the product was sol. in MeOH. This proved to be methyl pentamethyl-*m*-digallate m. 124-7°. This is the 1st time that this important building unit has been obtained directly from Chinese tannin. Attempts to hydrolyze methylotannin for the prepn. of this ester have failed so far. Judging from the yield of Me deriv. the MeO content and the sp. rotation, it is believed that Chinese tannin is a chem. individual. C. J. Wzsr

Preparation of benzenepentacarboxylic acid. KARL FLEISCHER AND HWAID RETZE. *Ber.* 56B, 228-34(1923).—The condensation of 2-ethyl-5,6,7,8-tetrahydronaphthalene with  $\text{Et}_2\text{C}(\text{COCl})_2$  by  $\text{AlCl}_3$  in  $\text{CS}_2$  gives 2,2,4-triethyltetrahydronaphth- $\alpha,\beta$ -indane-1,3-dione (I), m. 39°; the concd.  $\text{H}_2\text{SO}_4$  soln. is a pale yellow. Oxidation of I with fuming  $\text{HNO}_3$  by heating 7 hrs. in a sealed tube at 125-50° gave 2,2-diethylindane-1,3-dione-4,5,7-tricarboxylic acid (II), m. 249° (decompn.). If the heating is continued for 21 hrs. I gives a very good yield of  $\text{C}_6\text{H}(\text{CO}_2\text{H})_5$ . Reduction of I with Zn-Hg and HCl gave 2,2,4-triethyltetrahydronaphth- $\alpha,\beta$ -hydrindene (A),  $b_p$  203-5°,  $d_4^{20}$  0.9673,  $n_D^{20}$  1.5352. Condensation of A with  $\text{AcCl}$ , using  $\text{AlCl}_3$  in  $\text{CS}_2$ , gave the 5-acetyl derivative (B), needles, m. 66°. *p*-Nitrobenzaldehyde compound,  $\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}$ , canary-yellow needles, m. 161-5°. Reduction of B with Zn-Hg and HCl gave 2,2,4,5-tetraethyltetrahydronaphth- $\alpha,\beta$ -hydrindene (III),  $b_p$  220-2°,  $d_4^{27}$  0.9647,  $n_D^{27}$  1.5365.

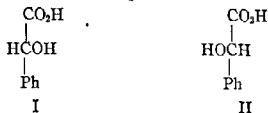


C. J. WEST

Condensation of  $\alpha$ -halogen ketones with aldehydes. SVEN BODFORSS. *Ber.* 55B, 3581(1922).—Bauer and Werner (757) have recently reported on the condensation of  $\alpha$ -halogen ketones with aldehydes, using halogen hydrides in presence of glacial HOAc as condensing agent. B. calls attention to his work in this field (*C. A.* 11, 2781; 13, 1713). E. H. VOLWILER

Configuration of mandelic acid and other  $\alpha$ -hydroxy acids. KARL FREUDENBERG, FRITZ BRAUNS, AND HEINRICH SIEGEL. *Ber.* 56B, 193-200(1923); cf. *C. A.* 16, 3871.—Clough (*C. A.* 12, 2188) reached the conclusion that mandelic acid from amygdalin possessed structure I. Hudson, applying his amide rule (*C. A.* 12, 1643), concluded that it possessed structure II. In order to decide between the 2 formulas, *dl*-hexahydro-mandelic acid was prepd. by reduction of the acid with Pt and H. Methyl ester,  $b_p$  122-3°. Phenylhydrazide, m. 213°. *d*(-)-hexahydro-mandelic acid, m. 128-9°,  $[\alpha]_{\text{H}_2\text{O}}^{25}$  in AcOH -26.6°,  $[\alpha]_{\text{H}_2\text{O}}^{27}$  -25.8°. Methyl ester,  $b_p$  123°,  $[\alpha]_{\text{H}_2\text{O}}^{25}$  -4.7°. Phenylhydrazide, m. 215°,  $[\alpha]_{\text{H}_2\text{O}}^{30}$  55.25°. Amide, m. 158°,  $[\alpha]_{\text{H}_2\text{O}}^{25}$  47.4° (in EtOH); in 20% EtOH 41.16°. *d*-Lactamide, m. 49-51°,  $[\alpha]_{\text{H}_2\text{O}}^{18}$  22.2°. Comparison of the rotations of

the HO acids and their amides in all cases where the *d*-structure had been established chem. showed that active mandelic acid possesses structure I. Hudson's amide rule



should thus read: If, upon transformation into its amide, the rotation of an  $\alpha$ -HO acid is increased towards the right the acid belongs to the *d*-series. A list of the known *d*-acids is given.

C. J. WEST

**Hydrogenated polycyclic ring systems. I. The hydrogenation of phenol and the resulting by-products.** WALTHER SCHRAUTH, WILHELM WEGE AND FRITZ DANNER. *Ber.* 56B, 260-8(1923); cf. *C. A.* 17, 280.—The fraction b. 270-80°, contained cyclohexenylcyclohexanol. The residue contained, as 1 constituent, 1,3-dicyclohexyl-2-cyclohexanone, m. 131-2°, long prisms, stable towards  $\text{KMnO}_4$  and giving no semicarbazone. Further hydrogenation at 180-90° gave 1,3-dicyclohexyl-2-cyclohexanol, needles, m. 117°, and an isomeric alcohol, b<sub>15</sub> 220-1°, slowly changing to the cryst. isomer (*cis*- and *trans*-forms?). The same acetate results from the 2 isomers, needles without sharp m. p. The oily alc., heated with  $\text{ZnCl}_2$  at 200-210° for 4 hrs., gave 1,3-dicyclohexyl- $\Delta^1$ -cyclohexene, b<sub>15</sub> 204-7°. A similar product was obtained from the solid isomer but it may consist of a mixt. of the 2 isomeric forms. This hydrocarbon was then reduced to the hexane,  $\text{C}_6\text{H}_{12}\text{C}_6\text{H}_{10}\text{C}_6\text{H}_{11}$ , long needles, m. 66-7°, the isomeric form of which b<sub>15</sub> 192-6°, d. 0.9335.

C. J. WEST

**Thermal decomposition of several hydroaromatic dicarboxylic acids.** A. WINDAUS, W. HUCKEL AND G. REVEREY. *Ber.* 56B, 91-8(1923).—In view of the fact that Blanc's rule (*C. A.* 1, 2561) is being used in establishing the constitution of hydroaromatic compds., it is desirable to det. in how far this rule holds with certainty. *cis*-Hexahydrohomophthalic acid, prisms, m. 146°; heated with coned.  $\text{HCl}$  5-6 hrs. at 200° in a sealed tube, the *trans*-acid was obtained, rosets of large crystals, m. 157°. Evapd. with  $\text{Ac}_2\text{O}$  both forms give anhydrides: *cis*, rectangular plates, m. 57°, *trans*, short needles and spears, m. 80-81°; upon heating with  $\text{H}_2\text{O}$ , the corresponding acid is regenerated. If either acid is evapd. with  $\text{Ac}_2\text{O}$ , the residue heated in an air bath to 240° and then distd. at 25 mm. a mixt. of the 2 anhydrides is obtained. An equil. mixt. of the 2 anhydrides contg. 25% *cis*- and 75% *trans*-anhydride, and m. 64-5°, is obtained by heating either anhydride for 12 hrs. at 220°. *cis*-Hexahydrohydrocinnamic-*o*-carboxylic acid, prisms and spears, m. 103°. Calcium salt, more difficultly sol. in hot than cold  $\text{H}_2\text{O}$ . Dianilide, glistening leaflets, m. 159°. *trans*-Acid, prisms, m. 143°; this acid is also obtained by distg. the *cis*-acid (260-300°). Dianilide, m. 212°. The *cis*-deriv. is transformed into the *trans*-deriv. by heating to 250°; the latter dists. without decompn. The *cis*-acid, evapd. with  $\text{Ac}_2\text{O}$  and then heated to 240-60°, gave hexahydro- $\alpha$ -hydrindone, b<sub>188</sub> 216°, d<sub>40</sub> 0.9982,  $n_D$  1.47915,  $n_D$  1.48117,  $n_B$  1.48827,  $n_Y$  1.49342; the odor resembles that of peppermint. Semicarbazone, needles, m. 214-5° (decompn.). Oxime, glistening needles, m. 79-80°.

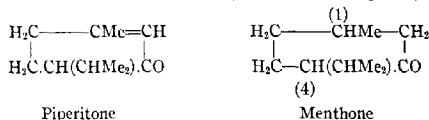
C. J. WEST

**Benzaurin.** RICHARD MEYER AND WILLY GERLOFF. *Ber.* 56B, 98-104(1923).—The deep red color of benzaurin (A) is not in harmony with the formula  $\text{HOCHPh}(\text{C}_6\text{H}_4\text{OH})_2$  originally proposed by Doebner (*Ann.* 217, 227). Analysis and mol. wt. detns. for the acetate confirm D.'s views that this is a diacetate. Further confirmation is found in the prepn. of the  *dibenzoate*, needles, m. 183-4°. Pure A could not be obtained by the sapon. of either deriv. nor by the oxidation of  $\text{HCPh}(\text{C}_6\text{H}_4\text{OH})_2$ . Decompn. of the perchlorate with  $\text{H}_2\text{O}$ , however, gave pure A, which analyzed for  $\text{C}_{19}\text{H}_{16}\text{O}_3$  but which is believed to be the hydrate of  $\text{C}_{19}\text{H}_{14}\text{O}_3$  (*p*-hydroxyfuchson). At 110-120°

1 mol.  $\text{H}_2\text{O}$  is lost. This idea is supported by the fact that the color of an alc. or  $\text{AcOH}$  soln. changes upon warming from a pale yellow to orange, probably because of the splitting off of the  $\text{H}_2\text{O}$ . *Benzaurin hydrochloride*, dark red needles. C. J. WEST

**The phellandrenes.** ERIC HURST, H. G. SMITH AND JOHN READ. *J. Proc. Roy. Soc., N. S. Wales* **56**, 176-9(1922).—*l*-Phellandrene  $\alpha$ -nitrite, m.  $121-2^\circ$  (decompn.), shows a remarkable mutarotation in org. solvents. In  $\text{CHCl}_3$   $[\alpha]_D^{20}$  after 8 min. was  $137.7^\circ$ , after 144 hrs.  $-70.0^\circ$ ; in  $\text{C}_6\text{H}_6$  after 5 min.  $234.4^\circ$ , after 355 hrs.  $-103.3^\circ$ ; in  $\text{MeAc}$  after 8 min.  $165.3^\circ$ , after 359 hrs.  $-38.1^\circ$ . A. W. DOX

**The stereoisomeric forms of menthone.** R. S. HUGHESDON, H. G. SMITH AND JOHN READ. *J. Proc. Roy. Soc., N. S. Wales* **56**, 170-5(1922).—*l*-Piperitone when hydrogenated in the presence of colloidal Pd gives *d*-isomenthone, and *d*-piperitone gives *l*-isomenthone. The menthones contain 2 asym. carbons of different rotatory power. When the menthone is prepd. from an optically active piperitone one of these asym. carbons (1) should be racemic while the other (4) should remain optically active. There



are thus 10 theoretically possible optical isomers of menthone. Representing the optical activity of carbon 1 by *d* or *l*, and that of carbon 4 by *D* or *L*, the isomers would be *Dd* and *Ll*, wholly uncompensated compds. (*d*- and *l*-isomenthones); *Dl* and *Ld*, partially internally compensated compds. (*d*- and *l*-menthones); *Dd*, *Dl* and *Ld*, *Ll*, partially racemic compds. (*l*-racemic isomenthones); *Dd*, *Ld* and *Dl*, *Ll*, partially racemic compds. (*d*-racemic isomenthones); *Dd*, *Ll* and *Ld*, *Dl*, wholly racemic compds. (*i*-isomenthone and *i*-menthone). A. W. DOX

**Phenylpyruvic ester.** H. GAULT AND R. WEICK. *Bull. soc. chim.* [4] **31**, 867-92, 993-1026(1922).— $\text{PhCH}_2\text{CN}$  and  $(\text{CO}_2\text{Et})_2$ , condensed with  $\text{NaOEt}$  (Erlenmeyer, *Ann.* **271**, 173(1892)), gave 80-85%  $\text{PhCH}(\text{CN})\text{COCO}_2\text{Et}$  (A). Hydrolysis of A with concd. and with slightly dild.  $\text{H}_2\text{SO}_4$  (the somewhat less detailed work of Bougault (*C. A.* **9**, 1048; **10**, 1984, etc.; Hemmerle, *Thesis, Paris* 1917) was not available to G. and W. until later) was rather completely studied.  $\text{PhCH}_2\text{COCO}_2\text{Et}$  (B) was made from 20 g. A, and 9 g.  $\text{H}_2\text{SO}_4$  (dild. with 1%  $\text{H}_2\text{O}$ ), let stand 24 hrs., 40 g. abs. alc. added, and heated at  $140^\circ$  for 1 hr. (autoclave). The yield was 91%, and the residue, phenylhydroxymaleic imide, can be converted into B. B, purified from polymers by 2 distns.,  $b_{15}$   $154.5^\circ$ . Crude B, from the autoclave, held 12 hrs. at  $-15^\circ$ , and seeded, gives about 50% of the  $\alpha$ -form (C), slender needles from ligroin, m.  $52^\circ$ . The filtrate from the C gives the  $\beta$ -form (D), liquid,  $b_{15}$   $152^\circ$ . D, let stand 48 hrs. with 2 parts satd.  $\text{NaOAc}$ , gave 33% of the  $\gamma$ -form (E), m.  $79^\circ$ , and 67%  $\text{PhCH}_2\text{C}(\text{CO}_2\text{Et}) \cdot \text{O} \cdot \text{CO} \cdot \text{CO} \cdot \text{CHPh}$  (F), m.  $140^\circ$ . E

is best prepd. from D with 4 parts of 10%  $\text{Cu}(\text{OAc})_2$  (41% yield).  $\text{FeCl}_3$  gives a green color in alc. with C and D, but not with E. C is oxidized after 2-3 hrs. in air, giving  $\text{BzH}$ ; D, after "some days"; E, not after 30 days. It is decided that C and D are *cis*- and *trans*-forms (which, undecided) and E is the keto form. Only C and D give compds. with  $\text{NaHSO}_3$ , but all give the same phenylhydrazone, m.  $89^\circ$ . C and D have normal mol. wts. in  $\text{PhH}$ , but E is normal only in dil.  $\text{HOAc}$  and double in  $\text{PhH}$ . Slow distn. at 15 mm. converts C or E to D, while  $\text{NaOAc}$  or  $\text{Cu}(\text{OAc})_2$ , converts D to E. Satd.  $\text{Na}_2\text{CO}_3$  changes either D or E to C. C or D brominated in  $\text{CS}_2$ ,  $\text{AcOH}$ , or  $\text{PhH}$ , gave  $\text{PhCHBrCOCO}_2\text{Et}$  (G),  $b_{15}$   $170^\circ$ ,  $b_{20}$   $182-4.5^\circ$ ; at  $-15^\circ$ , with excess of  $\text{Br}_2$ ,  $\text{PhCHBrC}(\text{OH})\text{BrCO}_2\text{Et}$ , solid, stable in air only at room temp. in excess of  $\text{HBr}$ . G does not react with cold  $\text{AcCl}$ , and gives a *phenylhydrazone*, m.  $106-8^\circ$  (decompn.), sol. in alc.,

but not in  $\text{CHCl}_3$ , ligroin, or  $\text{AcMe}$ .  $\text{HCl}$  and  $\text{HBr}$  do not react with **C**, but change **D** to **C**. **Hl** forms  $\text{PhCH}_2\text{CH}(\text{OH})\text{CO}_2\text{Et}$ ; *acetyl derivative*, oil,  $b_p$  161–3°; *benzoyl derivative*, fluorescent oil,  $b_p$  225–6°. The phenylurethan of **C** (or **D**), from the ester and  $\text{PhNCO}$  (allowed to stand 20 hrs.),  $m$ . 128.5°; in attempts to repeat the prepn. only once was a solid obtained. With  $\text{HCl}$  in alc., **C** and **D** give no **F**, even at 150°; but **E** yields **F** readily. All 3 readily yield **F** with  $\text{Na}_2\text{CO}_3$  or  $\text{NaOAc}$ . **E** with  $\text{Br}_2$  in boiling  $\text{CS}_2$  gave the *bromo derivative* of **F**,  $\text{PhCH}_2\text{C}(\text{CO}_2\text{Et})\text{O.CO.CO.CBrPh}$ ,  $m$ . 152°, slightly sol. in  $\text{EtOH}$

and  $\text{CS}_2$ , also made from **F** and  $\text{Br}_2$ . The following reactions are common to **C**, **D**, and **E**:  $\text{AcCl}$  at ordinary temp., no action;  $\text{Ac}_2\text{O}$  (boiled 1 hr.) gives the acetate of  $\alpha$ -hydroxycinnamic acid (**H**),  $m$ . 33.5°;  $\text{BzCl}$  and alkali give the corresponding *benzoyl derivative* (**J**), fine needles from alc.,  $m$ . 87°. Neither **H** nor **J** reacts with  $\text{PhN}_3\text{H}_3$ ;  $\text{Br}_2$  reacts by substitution, but no simple addn. products were formed; but both decolorize  $\text{KMnO}_4$  at once. With **C**, **D**, or **E**,  $\text{NH}_3$  gives the amide of **F**, or an unstable  $\text{NH}_4$  salt of **F**;  $\text{Et}_3\text{NH}$  gives only the salt of **F**, in this case more stable. Concd.  $\text{KOH}$  gives diphenylpyruvic acid,  $\text{PhCH}_2\text{C}(\text{OH})(\text{CO}_2\text{H})\text{CHPhCOCO}_2\text{H}$ ,  $m$ . 197°. **D** gives with  $\alpha\text{-C}_6\text{H}_4(\text{NH}_2)_2$  on standing, *N,N'*-dihydrobenzalquinoxalone, slightly yellow crystals from alc.,  $m$ . 210°. **D** condensed with  $\text{H}_2\text{CO}$  by  $\text{Et}_3\text{NH}$  gave *di-Et*  $\alpha,\alpha'$ -diketo- $\beta,\beta'$ -diphenylpimelate, non-distillable oil; with  $\text{PhN}_2\text{H}_3$ , it forms a *monophenylhydrazone*, very sol. in alc.,  $m$ . 162°, and a *diphenylhydrazone*, slightly sol.,  $m$ . 181°. Attempts to prep. isomeric forms of  $\text{BzCH}_2\text{COCO}_2\text{H}$ , were unsuccessful. The use of  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CN}$  for condensation with  $(\text{CO}_2\text{Et})_2$  gave products which could not be crystd.  $[\text{M}]_D^{20}$  in  $\text{PhMe}$ : **D**, 52.47; **E**, 50.90.

BEN H. NICOLET

The double bond of some ethylene derivatives of camphor obtained by catalytic hydrogenation. J. DETRIE. *Thesis Nancy* 1922, 45 pp.; *Chimie et industrie* 8, 1216 (1922).—A study of the phenomena of steric hindrance. D. hydrogenated mixts. of the various compds. under investigation with optically active compds. of the *aniscamphor* type. Hydrogenation occurs at both mols. simultaneously. The relative affinity of the  $\text{H}$  for the 2 mols. can be detd. polarimetrically. *Hexahydrobenzoylcamphor*,  $m$ . 27°, is obtained from hexahydrobenzoylbromide and "sodium camphor," or by complete hydrogenation of benzalcamphor. The various benzalcamphors are obtained by condensation of the aromatic aldehydes with "sodium camphor." A double bond between a  $\text{C}_6\text{H}_5$  nucleus and a side chain is more readily hydrogenated than one between 2 nuclei. The rate of hydrogenation of a double bond between 2 nuclei depends on the position of the substituted groups. If the substituted group is *o* relative to the C to which is attached the  $\text{C}_6\text{H}_5$  chain (methylsalicylcamphor), the rate of hydrogenation is lower than if it is *p* (aniscamphor). Hydrogenation of  $\text{PhOH}$  in the presence of Pt black gives a 80% yield of *cyclohexanol*. *Cyclohexanone* is formed as an intermediate product, and is detd. by means of its condensation product with 2 mols. of *piperonal*.

A. P.-C.

Reduction of the carbonyl group with zinc amalgam; theory of the reduction. WILHELM STEINKOPF AND ARTHUR WOLFRAM. *Ann.* 430, 113–61 (1923).—Reduction of  $\text{BzH}$  with  $\text{Zn}$  and aq.  $\text{HCl}$  at 90–5° gave fairly good yields of  $[\text{Ph}_2\text{C}(\text{OH})]_2$ . The use of 30 g.  $\text{Zn-Hg}$  in abs.  $\text{EtOH}$  and  $\text{HCl}$  gave rise to 7.5 g.  $(\text{Ph}_2\text{C})_2$ ; from 18.2 g.  $\text{BzH}$ , together with 3.5 g. almost pure  $\text{Ph}_2\text{CH}_2$ . The use of 15 g.  $\text{Zn-Hg}$  in the presence of alc.  $\text{HCl}$  gave 11 g. of  $\alpha$ - and  $\beta$ - $\text{Ph}_2\text{CCOPh}$ , while the use of larger amts. of  $\text{Zn-Hg}$  gave almost pure  $\beta$ -deriv. The reduction of  $\text{Ph}_2\text{CHOH}$  gave 82% of  $\text{Ph}_2\text{CH}_2$ . Four g.  $[\text{Ph}_2\text{C}(\text{OH})]_2$  gave 1.4 g.  $(\text{Ph}_2\text{C})_2$ , while this was obtained in 86% yield from  $\beta$ - $\text{Ph}_2\text{CCOPh}$ . 60 g.  $\text{AcCH}_2\text{CO}_2\text{Et}$  and 180 g.  $\text{Zn-Hg}$  with  $\text{HCl}$  gave 35 g. reduction product which contained  $\text{PrCO}_2\text{Et}$  and about 10% of  $\text{CH}_2\text{CHCH}_2\text{CO}_2\text{Et}$ ; some  $\text{MeCH}(\text{OH})\text{CH}_2\text{CO}_2\text{Et}$  was probably present.  $\text{CH}_2\text{CHCH}_2\text{CO}_2\text{Et}$  was not reduced under these conditions.  $\text{AcCH}_2\text{CH}_2\text{CO}_2\text{Et}$  gave  $\text{BuCO}_2\text{Et}$ , contg. 8–9% of unsatd. esters, in which the presence of

$\text{MeCH:CHCH}_2\text{CO}_2\text{Et}$  was established by conversion into the satd. HO deriv.  $\text{MeCH(OH)CH}_2\text{CH}_2\text{CO}_2\text{Et}$  could not be detected.  $\text{BzCH}_2\text{CO}_2\text{Et}$  gave 2,3-diphenylpentadilactone (C. A. 6, 3274) and  $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{Et}$ , besides a compound,  $\text{C}_{22}\text{H}_{20}\text{O}_6$ , b, 206–12°. The reduction of  $\text{BzCH}_2\text{CO}_2\text{Et}$  with ordinary Zn and HCl in EtOH gave a mixt. of  $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{H}$  and  $\text{PhCH:CHCO}_2\text{H}$ , besides 2,3-diphenylcrotonic lactone-3-acetic acid. 15 g.  $\text{PhCH:CHCO}_2\text{Et}$  gave 12.5 g. of the hydro ester. The reduction of  $\text{BzCO}_2\text{Et}$  at 20° gave *ethyl diphenyltartrate*, m. 116°, and  $\text{PhCH(OH)CO}_2\text{Et}$ ; at the b. p. of the alc.,  $\text{PhCH(OH)CO}_2\text{Et}$  and  $\text{BzOEt}$  were the only products. When  $\text{BzCO}_2\text{Et}$  was reduced with Zn and aq. HCl the only product isolated was  $\text{PhCH(OH)CO}_2\text{H}$ . With an excess of H (using aq. HCl and Zn-Hg)  $\text{BzMe}$  gave  $\text{PhCH:CH}_2$  and  $\text{PhCH}_2\text{Me}$ , together with  $\gamma$ -keto- $\beta,\beta$ -diphenylbutane (acetophenone pinacolin), compact crystals, m. 40–1°. Various polymerized forms of  $\text{PhCH:CH}_2$  were obtained. With 1 mol. H, the principal fraction was  $\text{PhEt}$ . In EtOH, the principal product was  $\text{PhCH:CH}_2$ .  $\text{BzH}$  gave  $\text{PhCH}_2\text{OH}$  and  $\text{PhMe}$  together with some stilbene and hydrobenzoin. The action of  $\text{ZnCl}_2$  upon  $\text{PhCH}_2\text{OH}$  gave  $\text{PhCH}_2\text{CHClPh}$ , besides a high boiling fraction.

C. J. WESR

**Benzilic acid rearrangement.** I. G. SCHEUING. *Ber.* 56B, 252–69(1923).—When benzil (A) and solid KOH are ground together and 5 cc.  $\text{C}_2\text{H}_5\text{N}$  then added, there is obtained a hard pale-yellow cake which is an addn. compd. of A and KOH. While  $\text{H}_2\text{O}$  immediately decomps. the compd. with liberation of benzil, very little can be dissolved out with  $\text{C}_2\text{H}_5\text{N}$ . That this compd. consists of 1 mol. of each of the components is rendered probable by the fact that KOH, pptd. from EtOH by  $\text{Et}_2\text{O}$ , reacts with A in these proportions, forming small pale yellow crystals.  $\text{H}_2\text{O}$  and EtOH decomp. the compd. into its components as does dry  $\text{CO}_2$ . Slow rearrangement to the acid takes place at 0°, almost immediately at 80°. The *potassium methylate-benzil complex*,  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{CH}_2\text{OK.C}_2\text{H}_5\text{O}$ , is nearly colorless and shows the same behavior as the KOH compd. Rearrangement, however, gives benzilic acid instead of the expected Me ester or  $\text{Ph}_2(\text{MeO})\text{CCO}_2\text{H}$ . The *sodium ethylate-benzil compound*, pale yellow crystals, does not contain alc. of crystn. This indicates that the addn. product is an intermediate step in the rearrangement. The violet color often observed is a side-reaction and the rearrangement may be carried out without any production of color. The nature of the color is unknown.

C. J. WESR

**The action of the alcohols on  $\alpha$ -bromobenzalacetophenone. Formation of various saturated and ethylenic compounds.** CH. DUFRAISSE AND P. GERALD. *Bull. soc. chim.* 31, 1285–1304(1922).—A more detailed account of the work reported in C. A. 16, 3312.

I. P. ROLF

**The  $\alpha$ -ethoxyquinaldines.** W. T. K. BRAUNHOLTZ. *J. Am. Chem. Soc.* 44, 2967(1922).—In connection with the statement of Gutekunst and Gray (C. A. 16, 3089) that they were able to find no reference to any method of prep. the 6-methoxy- and 6-ethoxyquinaldines, B. calls attention to his recent paper (C. A. 16, 1240).

C. A. R.

**Halochromism of fulgides.** HANS STOBBE AND RICHARD DIETZEL. *Ber.* 55B, 3567–80(1922).—Claisen and Ponder (*Ann.* 223, 142(1884)) first described halochromic compds. of the type of colored addn. products of strong acids and  $\alpha,\beta$ -unsatd. ketones. v. Baeyer and others considered them as true salts, whose stability toward hydrolysis varied according to the strengths of the acids and the “keto-bases.”  $\text{CCl}_3\text{CO}_2\text{H}$  salts are more deeply colored than the di-Cl, and these more than the mono-Cl salts. Absorption measurements in the visible spectrum of the ketones dissolved in halogen acids have also showed similar depths of color. Since fulgides also show halochromism, S. and D. investigated diphenylfulgide,  $\text{PhCH:C.CO.O.CO.C:CHPh}$ , and tri- and tetra-

fulgide (m. 219°). The color deepens with increased no. of Ph groups. When dissolved

in indifferent solvents, the same colors as those of the crystals themselves are produced. When dissolved in strong acids, such as the mono-, di- and trichloroacetic acids, the color is much deepened. Water causes hydrolysis of these salts, hence they cannot be isolated. Spectroscopic measurements were therefore made in soln. The light absorption increases with the strength of the acid, and is also dependent upon the chem. structure of the fulgide. The optical effect of the Ph group could be thus detd. Measurements of light absorption in the ultra-violet were also made and showed that the Ph group has no effect on these bands. The curves of the three halo acetic acid solns. in the case of each fulgide are parallel for each individual, the  $\text{CCl}_3\text{CO}_2\text{H}$  compd. having the lowest curve. The color factors in aryl-substituted fulgides consist of the *o*-quinonoid tetrahydrofuran nucleus,  $\text{=C:C.CO.O.CO:C=C=}$  and to a less extent depend on the

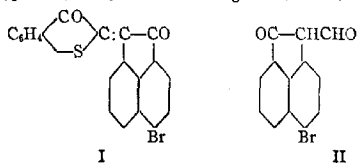
no. and nature of the aryl groups. Opening the ring or addn. of H to the 2 ethylenic groups causes loss of all or most of the color.

E. H. VOLWILER

**Preparation and rearrangement of the naphthyl ketoximes.** ERNST BECKMANN, OTTO LISSCHE and ERICH CORRENS. *Ber.* 56B, 341-54 (1923).—*Di-β-naphthyl ketoxime*, from the ketone and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in EtOH with or without NaOH on the  $\text{H}_2\text{O}$  bath or in a sealed tube at  $100^\circ$ , needles, m.  $180-1^\circ$ . Rearrangement with  $\text{PCl}_5$  in  $\text{Et}_2\text{O}$  (24 hrs.) gave *β-naphthoyl-β-naphthylamide*, glistening needles, m.  $239^\circ$ , identified by synthesis from  $\text{C}_{10}\text{H}_7\text{COCl}$  and  $\text{C}_{10}\text{H}_7\text{NH}_2$ . *Di-α-naphthyl ketoxime*, obtained only by heating the components in a sealed tube at  $135-40^\circ$  in 3% yield, small needles, m.  $200^\circ$ . Rearrangement gave  $\alpha\text{-C}_{10}\text{H}_7\text{CONHC}_{10}\text{H}_7$ , m.  $244^\circ$  (*Ber.* 1, 38). *α-Naphthyl-β-naphthyl ketoxime*, by heating the components in a sealed tube at  $135-40^\circ$  without addn. of alkali, m.  $171^\circ$ . Rearrangement gave *α-naphthoyl-β-naphthylamide*, needles, m.  $200^\circ$ , identified by synthesis from  $\alpha\text{-C}_{10}\text{H}_7\text{COCl}$  and  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$ . In the prepn. of the mixed ketone, the *magnesium complex*,  $\alpha,\beta\text{-(C}_{10}\text{H}_7)_2\text{C:NMgBr}$ , was isolated as yellow crystals, m.  $255^\circ$ .

C. J. WEST

**Acenaphthene series.** II. FRITZ MAYER and HEINRICH SCHONFELDER. *Ber.* 55B, 2972-4 (1922).—In a previous communication (*C. A.* 14, 2788) it was stated that acenaphthoquinone (A) was not acted upon by Br. M. and S. now report that A in  $\text{PhNO}_2$  at  $200^\circ$  when treated with Br gives naphthalic anhydride,  $\text{C}_{12}\text{H}_6\text{O}_4$ . The reaction does not occur when Br is used alone, or when  $\text{PhNO}_2$  is used alone or with Br in  $\text{PhCl}$ . Dry reagents are required. M. and S. were interested in ascertaining the location of the Br in Ciba-red R (I). With alc. KOH the dye gave *o*- $\text{C}_6\text{H}_4(\text{SH})\text{CO}_2\text{H}$  and II. 9 g. A in 20 cc. boiling  $\text{PhNO}_2$  were treated at  $200^\circ$  with 8 g. Br in 2 cc.  $\text{PhNO}_2$  by drops. HBr



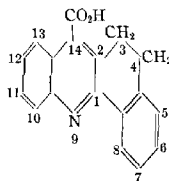
was evolved and the crystals which sepd. in the cold, crystd. from glacial HOAc, were naphthalic anhydride, m.  $270^\circ$ . An unsuccessful expt. using  $\text{PhCl}$  is described. 10 g. Ciba-red R, red needles from  $\text{PhNO}_2$ , dried *in vacuo* at  $140^\circ$ , m. above  $300^\circ$ , were refluxed in 100 g. alc., contg. 50 g. KOH. A green soln. resulted and after a short time the K salt of B sepd. The product after heating 2 hrs. was filtered and washed with alc. KOH. It was then dissolved in  $\text{H}_2\text{O}$  and 1-keto-2-aldehydo-5 (or 6)-bromoacenaphthene (II) was set free with acids, yellow to yellow-green flocculent product, very slightly sol. in alc.,  $\text{C}_6\text{H}_6$ , HOAc, and crystd. from  $\text{PhNO}_2$ , m.  $255^\circ$ . The alc. soln. of B gave a greenish blue color with  $\text{FeCl}_3$ . 2.8 g. B with 1 g.  $\text{PhNH}_2$  gave the *anil*, orange-

red needles from  $\text{PhNO}_2$ , m.  $175^\circ$ . The phenylhydrazone m.  $193^\circ$  (decompn.), yellow needles from  $\text{PhCl}$ . 3 g. **B** oxidized with 7 g.  $\text{Na}_2\text{Cr}_2\text{O}_7$  and 30 cc.  $\text{HOAc}$  as in the procedure used by Graebe (*Ann.* 327, 77(1903)) with bromoacenaphthene gave 4-bromonaphthalic anhydride, m.  $215^\circ$  (Graebe gives  $210^\circ$ ; the mixt. m.  $215^\circ$ ).  $\text{C}_6\text{H}_4(\text{SH})\text{CO}_2\text{H}$  was obtained from the reaction product of the  $\text{KOH}$  splitting of the dye by passing  $\text{HCl}$  into the alc. soln. for 12 hrs. and was identified by means of the  $\text{Et}$  ester, m.  $117\text{--}8^\circ$  (*Ber.* 31, 1670(1898); 32, 1150(1899)).

H. E. WILLIAMS

**Benzopolymethylene compounds. VI. Hydroxy bases and  $\beta$ -ketones of the tetralin and hydrindene series.** JULIUS V. BRAUN, OTTO BRAUNSDORF AND GEORG KIRSCHBAUM. *Ber.* 55B, 3648-63(1922); cf. *C. A.* 16, 4203.—*ac*- $\beta$ -Tetralylamine and its alkyl derivs. cause an increase in temp., in the animal body, while  $\alpha$ -HO- $\beta$ -NX<sub>2</sub> derivs. are relatively non-poisonous and lower the temp. On the other hand, alkoxyl derivs. are very poisonous and cause an increase in temp. This difference in physiol. action is probably due to the introduction of the alkoxyl group.  *$\alpha$ -Ethoxy- $\beta$ -dimethylaminotetralin*, pale yellow oil,  $b_{13}$   $152^\circ$ . The  $\text{HCl}$  salt is an oil, but the *picrate* m.  $199^\circ$  and the *methiodide*  $166^\circ$ . The base is stable when boiled with dil.  $\text{H}_2\text{SO}_4$  for several hrs.  *$\alpha$ -Ethoxy- $\beta$ -piperidinotetralin*  $b_{10}$   $170\text{--}2^\circ$ .  *$\alpha$ -Allyloxy- $\beta$ -diethylaminotetralin*  $b_{13}$   $165^\circ$ . Whether the HO or the  $\text{NH}_2$  group was in the  $\alpha$ -position to the aromatic nucleus was detd. by the reaction with  $\text{BrCN}$ , it being argued that the  $\beta$ - $\text{NH}_2$  must show a considerably greater stability towards  $\text{BrCN}$  than that in the  $\alpha$ -position.  *$ac$ - $\alpha$ -Piperidinotetralin*, prepd. from *ac*- $\alpha$ -aminotetralin and  $\text{Br}(\text{CH}_2)_5\text{Br}$ ,  $b_{17}$   $174\text{--}6^\circ$ ; the  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{MeI}$  salts are oils, the  $\text{Pt}$  salt is amorphous, but the *picrate* forms dark yellow needles, m.  $145\text{--}6^\circ$ . This readily reacts with  $\text{BrCN}$ , giving a mixt. of  $\Delta^1$ -dialin and piperidine. The  $\beta$ -derivative,  $b_{13}$   $186\text{--}7^\circ$ , gives a *hydrochloride*, m.  $230\text{--}1^\circ$ , a *hydrobromide*, m.  $233\text{--}4^\circ$ , a *methiodide*, m.  $209^\circ$ , and a *picrate*, m.  $203\text{--}4^\circ$ . This base reacts much less readily than its isomer, only 40% being reacted upon as compared with 75% in the 1st case. The  $\text{BzO}$  deriv. of the  $\beta$ -isomer reacts with  $\text{BrCN}$  with about 30% decompn. of the base, thus indicating its structure as a  $\beta$ -deriv.  *$ac$ - $\alpha$ -Hydroxy- $\beta$ -aminotetralin* is easily prepd. by shaking the hydroxybromide with 4 parts concd.  $\text{NH}_4\text{OH}$  for 30 hrs.; it  $b_{11}$   $160^\circ$ , m.  $109^\circ$ . *Hydrochloride*, nonhygroscopic, m.  $227^\circ$ ; *platinum salt*, m.  $215^\circ$ ; *picrate*, yellow leaflets, m.  $192^\circ$ ; *phenylthiourea*, m.  $134^\circ$ ; *benzylidene compound*, m.  $115^\circ$ ; *salicylidene compound*, m.  $108^\circ$ .  *$N$ -Acetate*, m.  $203^\circ$ .  *$N$ - $p$ -Nitrobenzoate*, m.  $228^\circ$ .  *$p$ -Aminobenzoate*, m.  $208^\circ$ , the *hydrochloride* of which m.  $239^\circ$ .  *$\alpha$ -Hydroxy- $\beta$ -[ $\beta'$ -hydroxyethylamino]tetralin*,  $b$   $190\text{--}6^\circ$ , the *hydrochloride* of which m.  $155^\circ$ .  *$\beta$ -Benzylamino derivative*,  $b_{13}$   $243\text{--}6^\circ$ ; *picrate*, m.  $192^\circ$ ; *hydrochloride*, m.  $237^\circ$ .  *$\beta$ -Nortropyl derivative*,  $b_{14}$   $210\text{--}2^\circ$ ; *picrate*, m.  $174^\circ$ ; the *hydrochloride* is hygroscopic. The  $\beta$ - $\text{NMe}_2$  deriv. gives a *picrate* m.  $138^\circ$  and a *methiodide*, m.  $138\text{--}9^\circ$ .  *$p$ -Nitrobenzoate*, m.  $112^\circ$ , is reduced by  $\text{ZnCl}_2$  to the *p*-aminobenzoate, m.  $137^\circ$ . The  $\text{MeI}$  salt, heated a few degrees above its m. p., splits off  $\text{Me}_3\text{NHI}$ , yielding  $\beta$ -tetralin,  $b_{10}$   $130^\circ$ ,  $d_4^{16.9}$  1.1055. The oxime m.  $89^\circ$ , the phenylhydrazone at  $109^\circ$  and the *semicarbazone* at  $190\text{--}1^\circ$ .  *$ac$ - $\alpha$ -Hydroxy- $\beta$ -dimethylaminohydrindene*,  $b_3$   $153\text{--}6^\circ$ , m.  $62^\circ$ . *Hydrochloride*, m.  $183\text{--}4^\circ$ ; *picrate*, m.  $145^\circ$ ; *methiodide*, m.  $161\text{--}2^\circ$ . Heated slightly above its m. p., the  $\text{MeI}$  deriv. gives  $\beta$ -hydrindene. VII. Pharmacological analogs of *ac*- $\beta$ -aminotetrahydronaphthalene. J. V. BRAUN, HEINRICH GRUBER AND G. KIRSCHBAUM. *Ibid* 3664-74.— $\beta$ -Aminotetrahydronaphthalene (**A**) shows a peculiar physiol. behavior when compared with other compds. contg. an  $\text{NH}_2$  group in the  $\beta$ -position to an aromatic nucleus, in that it not only increases the blood pressure but increases the body temp. The present work was undertaken to establish whether this was a peculiarity of the chem. compn. of **A**, or whether the  $\text{NH}_2$  group in the  $\beta$ -position to an aromatic or a hydroaromatic group would show the same behavior. *2-Phenylcyclohexylamine*,  $b_{12}$   $133\text{--}4^\circ$ , m.  $59\text{--}60^\circ$ , was prepd. by the reduction of 2-phenylcyclohexanone oxime (*C. A.* 9, 614)

with Na and EtOH. The hydrochloride m. 253°; the chloroplatinate forms reddish yellow needles and m. 222° (decompn.). Acetate, m. 130°; phenylthiourea, m. 185°; methiodide, glistening leaflets, m. 235°. The ketone was prepd. by the oxidation of the alc. mixt. which was obtained by the reduction of  $\text{PhC}_6\text{H}_4\text{OH}$  with H and Ni under pressure. The base raises the blood pressure, but has no other analogy to A. *ac*- $\alpha$ -Amino-methyltetralin was prepd. according to Bamberger (*Ber.* 20, 1703). The hydrochloride m. 230°, the picrate at 170° and the benzoate at 125–6°. An attempt was made to prep. the base from tetralin and  $\text{BrCH}_2\text{CO}_2\text{Et}$ , which gave an unsatd. ester,  $\text{C}_{14}\text{H}_{13}\text{O}_2$ ,  $b_{14}$  183–4°. The acid,  $\text{C}_{13}\text{H}_{12}\text{O}_2$ , needles, m. 100°, may be reduced by H and Pd to  $\alpha$ -tetralylacetic acid, m. 35–6°. The amide gave only a very small yield of the amine by Hofmann's reaction and the method was discarded in favor of B.'s original method. The action of  $\text{PCl}_5$  upon the Bz deriv. of *ar*- $\alpha$ -tetralylmethylaniline, m. 144°, gave  $\alpha$ -tetralylmethyl chloride,  $b_{13}$  144–5°, m. 150–1°. The  $\beta$ -chloride  $b_{13}$  141–2° but did not solidify.  $\alpha$ -Nitrile, needles,  $b_{10}$  168–9°, m. 69–70°. *ar*- $\alpha$ -[ $\beta'$ -Aminoethyl]tetralin, by reduction of the nitrile,  $b_{14}$  146–9°. Hydrochloride, m. 245°; picrate, small leaflets, m. 231°; benzoate, long spears, m. 123°. The physiol. properties are similar to those of A. VIII. Cyclic analogs of atophan. J. v. BRAUN AND PAUL WOLFF. *Ibid* 3675–83.—The condensation of isatin and  $\alpha$ -tetralone by means of KOH proceeds smoothly and gives an 80% yield of 3,4-dihydro-1,2-naphthacridine-14-carboxylic acid (tetraphan) (A),



fine light yellow needles, m. 252° ( $\text{CO}_2$  evolution). Sodium salt, apparently contains  $\text{H}_2\text{O}$  of crystn. lost in the air. Lead salt, pale yellow; copper salt, silver salt, stable in the light. Ethyl ester, long, compact needles, m. 80°. Heated above its m. p., A gives a practically quant. yield of 3,4-dihydro-1,2-naphthacridine (B),  $b_{10}$  237–8°, m. 60°. Hydrochloride, long needles, m. 226°; picrate, m. 206°; methiodide, reddish yellow powder, m. 191° (decompn.). 1,2-Naphthacridine is readily obtained from this base by heating with  $\text{PbO}$  1 hr. at 300–20°. Oxidation with  $\text{CrO}_3$  leads to 1,2-naphthacridine-3,4-quinone, orange powder, m. 242°. While it is relatively easy to dehydrogenate B, it is more difficult in the case of A; this is best accomplished by heating 10 g. A with 100 cc.  $\text{AcOH}$  and 6 g. Br for 2 hrs. at 120–30°; 1,2-naphthacridine-14-carboxylic acid (dehydrotetraphan) forms a fine yellow powder from alc., m. 261°. The cobalt salt is orange-yellow, the copper salt green, the mercury salt light yellow. The silver salt is a dirty yellow quickly turning to a greenish brown in the sunlight. Methyl ester, m. 83°. Heated above its m. p., the acid gives 1,2-naphthacridine. Reduction of A with Na and EtOH or  $\text{AmOH}$  gives [1,2-naphthacridine-1,2,3,4,9,1,4-hexahydro]-14-carboxylic acid (tetrahydrotetraphan), m. 190°. Nitroso compound, m. 149°. Acetate, m. 247°. 10-Methyl-3,4-dihydro-1,2-naphthacridine-14-carboxylic acid (o-methyltetraphan), by the condensation of o-methylisatin with  $\alpha$ -tetralone, m. 188° with evolution of  $\text{CO}_2$ , giving 10-methyl-3,4-dihydro-1,2-naphthacridine,  $b_{10}$  248–53°, m. 93–4°. Picrate, reddish yellow m. 141°; hydrochloride, long pale yellow needles, m. 173°. 10-Methyl-1,2-naphthacridine, m. 107°; picrate, m. 155°; hydrochloride, m. 136°. 12-Methyl-3,4-dihydro-1,2-naphthacridine-14-carboxylic acid (12-methyltetraphan), m. 239°. The 12-chloro derivative is light yellow and m. 283°, forming 12-chloro-3,4-dihydro-1,2-naphthacridine,  $b_{11}$  257–62°,



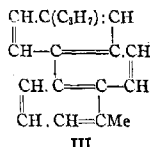
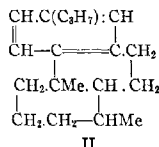
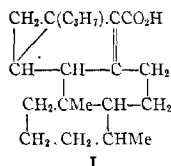
m. 102°. *Hydrochloride*, m. 240°. Treatment with PbO splits off the Cl as well as the H, so that dihydronaphthacridine results. The 12-bromo derivative is light yellow and m. 265°. *Methyl ester*, glistening yellow leaflets, m. 128°. 12-Bromo-3,4-dihydro-1,2-naphthacridine, pale yellow needles, m. 168°. The condensation of isatin with octahydrophenanthrene  $\alpha$ -ketone (not yet described by Schroeter) gives 7,8-tetramethylene-3,4-dihydro-1,2-naphthacridine-14-carboxylic acid, m. 210° (decompn.).  $\alpha,\alpha'$ -Acenaphthyl- $\gamma$ -cinchonic acid, from isatin and acetylacenaphthene, yellow, m. 234°. *Tetramethylenestophan* was obtained by warming an alc. soln. of tetralylamine, BzH and  $\text{AcCO}_2\text{H}$ , yellow, m. 260°. The pharmacol. behavior will be published separately.

C. J. WEST


The molecular refraction of anthracene. F. KROLLPFIEFFER. *Ber.* 56B, 77-83 (1923).—v. Steiger (*C. A.* 17, 380) found the mol. refraction of  $\text{C}_{14}\text{H}_{10}$  dissolved in  $\text{C}_{10}\text{H}_8$  to be 59.69. K. in some recent work with  $\text{C}_9\text{H}_7\text{N}$  found an av. value of 65.3. Repetition of S.'s expt. with carefully purified  $\text{C}_{14}\text{H}_{10}$  gave values agreeing with K.'s earlier value. That this should be so is confirmed by expts. with 1-Me $\text{C}_{10}\text{H}_8$  and 9-Et $\text{C}_{10}\text{H}_8$  in  $\text{C}_{10}\text{H}_8$ , the values for  $[\text{M}]_D$ , 69.71 and 74.84, agreeing well with those found for the molten compd., 69.35 and 74.17.  $[\text{M}]_D$  for phenanthrene in  $\text{C}_6\text{H}_6$  and  $\text{C}_9\text{H}_7\text{N}$  agreed well with those found by S. in  $\text{C}_{10}\text{H}_8$ .


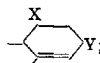
C. J. WEST




Coniferous resin acids. V. The nitrosochloride, nitrosite and nitrosate of pinabietic acid and abietic acid (Levy) and of abietin. Constitution of abietic acid. OSSIAN ASCHAN. *Ber.* 55B, 2944-59 (1922).—Investigations on the resin acids,  $\text{C}_{20}\text{H}_{30}\text{O}_2$ , date from 1824 (Unverdorben) but during the last century little information has been added, the matter being complicated by the difficulties involved in obtaining pure material. Vesterberg (*Ber.* 18, 3331 (1885); 19, 2167 (1886); 20, 3248 (1887); 36, 4200 (1903)) worked on pimaric acid. Mach (*Monatsh.* 14, 187 (1889); 15, 627 (1894)) worked in this field but on impure material ( $\text{C}_{19}\text{H}_{28}\text{O}_2$ ). Levy (*C. A.* 4, 454) prepd. from American rosin a pure abietic acid (B), m. 182°. Johansson (*Arkiv Kemi, Min. Geol. Stockholm.* 5, No. 6 (1917)), using superheated steam obtained an abietic acid m. 168-73°,  $[\alpha]_D$  -28.6° in alc., resembling pinabietic acid (A) prepd. by A. as pointed out also by Virtanen (*C. A.* 15, 3096). A was obtained from the so-called "Spruce oils" (*Kieferöl*, Swedish *Tallolja*) which were obtained by steam distn. of the acidified black liquor from the sulfate process. Virtanen's work points to the formula of A as I. The acid chloride yields on loss of  $\text{CO}_2$  and HCl pinabietin,  $\text{C}_{19}\text{H}_{28}$  (II), which when heated with S gives retene (III) (Bucher, *C. A.* 4, 1465), which with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$  gave trimellitic acid, 1,2,4- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$ . According to I, a  $\text{CO}_2\text{H}$  group and a 3-membered ring and a double



bond are in a 6-membered ring which also bears an iso-Pr group. Proof for the position of the groups relative to the iso-Pr group has been lacking. Numerous other formulas for A may be written. Hitherto it was impossible to tell whether Levy's B, which closely resembles A, was structurally different from it or isomeric with it. Both acids react with NOCl and with nascent  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$ , as do the terpenes. The equation  $\text{C}_{20}\text{H}_{32} + 3\text{O} = \text{C}_{20}\text{H}_{30}\text{O}_2 + \text{H}_2\text{O}$  shows the relationship between these acids and the diterpenes. Levy stated that B contains 2 double bonds, because by an alk.  $\text{KMnO}_4$  oxidation he obtained a tetra-HO compd.,  $\text{C}_{20}\text{H}_{30}(\text{OH})_4\text{O}_2$ . By the same treatment A

did not yield a similar product in the hands of Virtanen and he concluded from chem. and refractometric detns. that **A** has only one double bond and has a cyclopropane ring, both in the 6-membered ring which contains the iso-Pr and CO<sub>2</sub>H groups. In the case of the 6-membered ring as in **A** the 6 members when arranged as  may add

XY to give  or the cyclopropane ring may be split yielding 

in case there are 2 double bonds in the ring as in the case represented by  then on adding XY the cases are  and . Johansson found that the **B**

from American rosin took up only 2 atoms of H and that the dihydro acid was satd. **A** according to Virtanen behaves similarly. Consequently Levy's **B** contains the iso-Pr, the CO<sub>2</sub>H and the unsatd. group in 1 and the same 6-membered ring of a completely hydrogenated phenanthrene ring. The positions of the Me groups in the side chains are identical with those of the same groups in **A**. Levy observed that **B** with KMnO<sub>4</sub> in the cold takes up 4 OH groups with formation of a high melting well crystd. tetra-HO acid according to the equation  $C_{19}H_{29}CO_2H + 2H_2O + 2O = C_{19}H_{25}(OH)_4CO_2H$ . **A**, and also Virtanen tried to oxidize **A** under all sorts of conditions but no high melting product difficultly sol. in Me<sub>2</sub>CO could be found. **A**. repeated Levy's work and obtained the same oxidation product from Levy's **B** as from **A** and the last argument against the structural identity of these 2 acids is removed. Levy's **B** was impure. The nitrosochlorides, nitrosites and nitrosates of **B** are not direct derivs. of **B** but belong to the silvinic acid series of Wienhaus. *Pinabietic acid nitrosochloride* (**C**) was prepd. by heating 5 g. **A** with a mixt. of 10 g. EtNO<sub>2</sub> and 10 g. glacial HOAc. The mixt. was cooled by the use of ice and salt. 1.2 cc. concd. HCl was added to the reaction mixt. by drops during 0.5 hr. **C** sep'd. at once and after standing 2 hrs. was filtered and washed with MeOH. Additional amts. of HCl added to the filtrate did not cause further pptn. of **C**. The mother liquors contained a brown amorphous yellow mass. The use of 7 g. EtNO<sub>2</sub> instead of 10 did not increase the yield, nor did the use of gaseous HCl. The yield was increased when AmNO<sub>2</sub> was used, the best yields resulting when 25 g. **A** in 50 g. AmNO<sub>2</sub> and 22 g. glacial HOAc were treated with gaseous HCl; 4.8 g. (19% yield) pure **C** resulted. **C** pptd. from CHCl<sub>3</sub> by petr. ether m. 140° (foaming), by repeated dissoln. and repptn. shining needles m. 144-5°, easily sol. in CHCl<sub>3</sub> and C<sub>6</sub>H<sub>6</sub>, in boiling MeOH and alc., difficultly sol. in petr. ether. It gives a *sodium salt* with Na<sub>2</sub>CO<sub>3</sub>. The soln. decolorizes KMnO<sub>4</sub> at once. When 10 g. **C** was refluxed 3 hrs. with 1.4 g. Na in 35 cc. 90% alc. NaCl sep'd. Water was added to dissolve the NaCl and when H<sub>2</sub>SO<sub>4</sub> was added *nitrosoabietic acid* was pptd., amorphous product which on rubbing became cryst. The dry product dissolved completely in C<sub>6</sub>H<sub>6</sub> and was pptd. again with petr. ether as a gel which gradually became cryst., light brownish yellow powder, sintering at 120° and decomp. 130°, sol. in C<sub>6</sub>H<sub>6</sub>, easily sol. in CHCl<sub>3</sub>, difficultly sol. in MeOH and almost insol. in petr. ether, sol. in Me<sub>2</sub>CO, the soln. decolorizing KMnO<sub>4</sub>. 50 g. **A** in 300 g. C<sub>6</sub>H<sub>6</sub> were placed in a flask over a soln. of 50 g. NaNO<sub>2</sub> in 200 cc. H<sub>2</sub>O. Concd. HCl (70 g.) was dropped into the mixt. during several hrs., the mixt. being cooled in ice, and let stand overnight at 0°. Later 50 g. NaNO<sub>2</sub> in 200 cc. H<sub>2</sub>O with 70 g. HCl were added, and after further standing, the C<sub>6</sub>H<sub>6</sub> layer was sep'd., and the C<sub>6</sub>H<sub>6</sub> distd. at room temp. The sirupy residue was rubbed in petr. ether and purified by dissolving it in C<sub>6</sub>H<sub>6</sub> followed by pptn. with petr. ether. *Pinabietic acid nitrosite* (**D**) forms fine light greenish crystals, sintering 75-8°, sol. in C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub>, MeOH, alc., Et<sub>2</sub>O, Me<sub>2</sub>CO,

EtOAc and HOAc. It is sol. in  $\text{Na}_2\text{CO}_3$  and is thrown out again with acids (m.  $77-8^\circ$ ). After heating a 10%  $\text{C}_6\text{H}_6$  soln. on the oil bath for 3 hrs. **D** is stable, m. after crystn.  $76-77^\circ$  with no gas evolution. To 50 g. **A** in 50 g.  $\text{AmNO}_2$  and 65 g. HOAc, 44 g. concd.  $\text{HNO}_3$  were added by drops with const. shaking. The liquid was cooled during the treatment to  $-15^\circ$ . The mixt. was kept for 3 hrs. in the cold and then allowed to rise to  $0^\circ$  overnight after which 50 g. HOAc additional were added. To the yellow soln. smelling of AmOH, 260 cc.  $\text{H}_2\text{O}$  were added, and the lower layer was sepd., washed with  $\text{H}_2\text{O}$ , dried with  $\text{CaCl}_2$  and allowed to stand. Petr. ether threw out a thick mass which in  $\text{C}_6\text{H}_6$  was thrown out with petr. ether. In this way 29.8 g. *pinabietic acid nitrosite* (**E**), decomp.  $75-6^\circ$ , was obtained. Further treatment lowered the decompn. point to  $72-3^\circ$ ; it is a yellow powder, whereas **D** is greenish, and the soly. of **E** resembles that of **D** in the diverse solvents. **E** seps. from  $\text{H}_2\text{SO}_4$  unchanged. The Liebermann reaction with  $\text{PhOH}$  and  $\text{H}_2\text{SO}_4$  could not be obtained. **E** forms salts in soda and reduces  $\text{KMnO}_4$ . **B**, m.  $181-3^\circ$ , was prepd. according to Levy's method from American rosin. Since the purification involved much loss of material, an impure product was used in this work (m.  $167-70^\circ$ ). From 3.7 g. **B** 0.51 g. of abietic acid nitroschloride was obtained and a mixt. of this product and **C** m.  $139-40^\circ$ . A mixt. of abietic acid nitrosite and **D** decompd.  $76^\circ$ . Abietic acid nitrosate when mixed with **E** sintered  $72^\circ$ . A table is given showing the behavior of **B** and **A** when (I) treated with concd.  $\text{H}_2\text{SO}_4$  with a drop of  $\text{PhOH}$  in  $\text{H}_2\text{SO}_4$ , (II) with concd.  $\text{HNO}_3$ , heated on the steam bath and then moistened with  $\text{NH}_4\text{OH}$ , (III) in  $\text{CHCl}_3$  with  $\text{Ac}_2\text{O}$  and concd.  $\text{H}_2\text{SO}_4$  in the cold, and (IV) with cold concd.  $\text{HNO}_3$ . The results of the investigation show that **A** and **B** are identical.

H. E. WILLIAMS

A new compound from coniferous wood distillates. KARL CEDERQVIST AND BROR HOLMBERG. *Ber.* 56B, 298-300(1923).—In the distn. of MeOH from an alk. pyroligneous mixt. obtained from a mixt. of 80% pine and 20% fir wood, a deposit of fine needles was noticed in the condenser. Distn. with steam gave a compound,  $\text{C}_{12}\text{H}_{18}\text{O}$ , b. about  $258^\circ$ , m.  $69-70^\circ$ , and forming flat, slightly glistening prisms, 5-6 mm. long and 1-2 mm. wide. It is optically inactive, and gives a *semicarbazone*, flat needles or thin prisms, m.  $198-9^\circ$ , and an *oxime*, flat, needle-like prisms, m.  $110-3^\circ$ . The compd. is attacked by Br in  $\text{CHCl}_3$  but is only slowly oxidized by  $\text{HNO}_3$ ,  $\text{KMnO}_4$  or  $\text{Br}-\text{H}_2\text{O}$ .

C. J. WEST

Constitution of spruce-lignin. III. PETER KLASON. *Ber.* 56B, 300-8(1923); cf. *C. A.* 16, 2480.—After the  $\alpha$ -lignin is pptd. from 3 l. fresh waste liquor by 60 g.  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2\cdot\text{HCl}$  and removed by filtration, the liquor is concd. at  $30^\circ$  to about 1 l. and the  $\text{H}_2\text{SO}_4$  quant. removed by  $\text{BaCl}_2$ . After further concn., the Ca salt of the  $\beta$ -ligninsulfonic acid may be pptd. with MeOH. After repptn. of the salt, the salt is pptd. by  $\text{C}_{10}\text{H}_7\text{NH}_2$  and extd. with  $\text{H}_2\text{O}$  until no trace of Cl is present. This then analyzes for  $\text{C}_{19}\text{H}_{19}\text{O}_7\cdot\text{H}_2\text{SO}_4\cdot 2\text{C}_{10}\text{H}_7\text{NH}_2$  ( $\text{C}_{39}\text{H}_{38}\text{O}_{14}\text{N}_2\text{S}$ ), and differs by 2 O from the 1st formula proposed. The hypothesis is advanced that the  $\beta$ -lignin results through the condensation of 1 mol. coniferyl aldehyde (**A**) with 1 mol. caffeic acid. In an attempt to synthesize **A** from vanillin, AcOH and 10% NaOH, a small amt. of an amorphous product was obtained which is considered as a dimeric **A** and is believed to be identical with *hemiacrolein-lignin*, a term applied to lignin which has been treated with alkali and which is insol. in sulfite liquor. The same compd. appears to result from the oxidation of coniferyl alc. In 1 expt. in which the alc. was prepd. by means of emulsin, and allowed to stand for some time, a powder sepd. which, when cooked with sulfite liquor and then pptd. with  $\text{C}_{10}\text{H}_7\text{NH}_2$ , gave a product apparently identical with acrolein-lignin.

C. J. WEST

Hydroxypyrrrole derivatives. II. ERICH BENARY AND RUDOLF KONRAD. *Ber.* 56B, 44-52(1923); cf. *C. A.* 7, 2573.—Ethyl  $\alpha$ -chloroacetyl- $\beta$ -anilinoacrylate (**A**), by

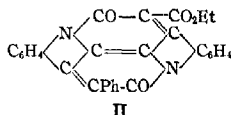
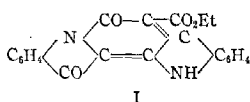
the action of  $\text{ClCH}_2\text{COCl}$  upon  $\text{PhNHCH:CHCO}_2\text{Et}$  in  $\text{C}_6\text{H}_6\text{N}$ , felt-like needles, m.  $83^\circ$ , and decomp. above  $200^\circ$  with gas evolution. Some of the isomeric *N*-chloroacetyl ester also resulted, sepd. by its insoly. in  $\text{C}_6\text{H}_6$ , prisms, m.  $136-7^\circ$ . Rubbing 2 g. A with 1 g. KOH in 5 cc. EtOH gave an 80% yield of *ethyl 1-phenyl-3-hydroxypyrrrole-4-carboxylate* (B), felt-like needles, m.  $83-4^\circ$ . The alc. soln. gives an intense blue color with  $\text{FeCl}_3$ , quickly changing through brown to green. A pine stick moistened with HCl is colored violet-red. 10% alc. KOH gives the *free acid* (B), small rods, m.  $172-4^\circ$  (decompn.). Alc.  $\text{FeCl}_3$  gives a greenish blue color, changing through green to brownish violet. B, warmed with  $\text{AmNO}_2$  on the  $\text{H}_2\text{O}$ -bath, gives *ethyl 1-phenyl-2-isonitroso-3-ketopyrrolino-4-carboxylate*, citron-yellow, 6-sided prisms, decomp.  $185^\circ$ . The action of  $\text{NaNO}_2$  upon the AcOH soln. of the ester gave an *isomeric ester*, compact needles, m.  $167-8^\circ$ . B, heated with  $\text{AcONa}$  and  $\text{Ac}_2\text{O}$ , gives the *3-acetoxy derivative*, needles, m.  $145-7^\circ$ . A, in NaOH soln., treated with  $\text{PhN}_2\text{X}$ , gives *ethyl 1-phenyl-2-benzeneazo-3-hydroxypyrrrole-4-carboxylate*, soft, orange-yellow needles, m.  $170-2^\circ$ .  $\text{FeCl}_3$  in EtOH gives a blood-red color. The *free acid* forms orange needles, m.  $185-7^\circ$ . *1-Phenyl-3-methoxypyrrrole-4-carboxylic acid*, leaflets, m.  $166-7^\circ$  (decompn.). Heated *in vacuo* at  $180-200^\circ$ , this acid loses  $\text{CO}_2$ , giving *1-phenyl-3-methoxypyrrrole*, needles, m.  $33-4^\circ$ . The action of KOH upon  $\text{MeC}(\text{NHPh})\text{:C}(\text{COAc})(\text{COCH}_2\text{Cl})$  gives *methyl 1-phenyl-3-hydroxy-5-methylpyrrole-4-carboxylate*, small pale rose needles, m.  $123-4^\circ$ . The ester gives a brick-red pine reaction and a dark green color with  $\text{FeCl}_3$ . The *free acid* forms needles, m.  $145^\circ$ . The *2-isonitroso-3-keto derivative* of the ester forms pale yellow needles, m.  $185-7^\circ$ . The corresponding *acid* is obtained as yellow needles, decomp.  $171-2^\circ$ .  $\text{NaNO}_2$  in AcOH, acting upon the Me ester, gives *methyl 1-phenyl-2-nitrimino-3-keto-5-methylpyrrolino-4-carboxylate*, orange needles, decomp.  $192-3^\circ$ . C. J. WESS

**Action of diazomethane upon dyestuffs and several nitrotyrroles.** WILLIAM KÖSTER and WILHELM MAAG. *Ber.* 56B, 55-69 (1923).—The addn. product of  $\text{CH}_2\text{N}_2$  to bilirubin ester (C. A. 16, 3674) contains 3 MeO groups, 2.25 of which are split off at  $140^\circ$ , the remainder at  $270^\circ$ . The action of  $\text{CH}_2\text{N}_2$  upon a suspension of pure bilirubin and the  $\text{NH}_4$  compd. in abs. EtOH at  $23^\circ$  gives the same compd.,  $\text{C}_{32}\text{H}_{42}\text{O}_9\text{N}_6$ ; at 1 mm. the N of the  $\text{CH}_2\text{N}_2$  is given off. The "indigo" compd. (Benary, C. A. 7, 2573) gives a red *resin* with  $\text{C}_6\text{H}_5\text{N}$  which analyzes for  $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_2 \cdot 2\text{H}_2\text{O}$ , and contains 7.54% Me and 14.28% Et. 2,4'-[5-Methyl-4-carbethoxy-3-pyrrolone]-3'-acetyltetronic acid,  $\text{C}_{14}\text{H}_{16}\text{O}_6\text{N}$ , from acetyltetronic amide and chloroacetylaminocrotonic ester by the action of alc. KOH, yellow needles from EtOH, m.  $190^\circ$  (decompn.). Alc.  $\text{FeCl}_3$  gives a dark brown coloration. It may be recovered unchanged from an alk. soln. after boiling.  $\text{CH}_2\text{N}_2$  forms a reddish brown *resin*,  $\text{C}_{16}\text{H}_{19}\text{O}_4\text{N}$ , insol. in alkali but sol. in HCl with a yellow color. The  $\text{FeCl}_3$  reaction is negative. 2,2'-Bis-[3-keto-5-methyl-4-carbethoxypyrrrole]-hydrate likewise forms a yellow *resin* with  $\text{CH}_2\text{N}_2$ , which analyzes for  $\text{C}_{18}\text{H}_{24}\text{O}_8\text{N}_4$ . [3-Hydroxy-5-methyl-4-carbethoxypyrrrolenyl-2]-furylmethane forms a *hydrochloride*,  $\text{C}_{13}\text{H}_{11}\text{O}_4\text{NCl}$ , reddish brown needles, immediately decompd. by HCl.  $\text{CH}_2\text{N}_2$  gives a dark brown *resin*,  $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}_3$ ; a part of the N of the  $\text{CH}_2\text{N}_2$  is split off upon drying at  $70^\circ$ ; the  $\text{FeCl}_3$  reaction is positive. [3-Hydroxy-5-methyl-4-carbethoxypyrrrolenyl-2]-*o*-hydroxyphenylmethane, brownish yellow needles, m.  $207^\circ$  (decompn.).  $\text{FeCl}_3$  gives a dark brown color. This readily reacts with  $\text{CH}_2\text{N}_2$ , giving a yellow *resin*,  $\text{C}_{17}\text{H}_{19}\text{O}_4\text{N}_3$ , which contains 6.53% N after drying 4 hrs. at  $25^\circ$  and 1 mm. *Carbethoxymaleinimide* was prepd. by the oxidation of 2,5-dimethyl-3-carbethoxypyrrrole with  $\text{CrO}_3$  in  $\text{H}_2\text{SO}_4$ , needles, m.  $115^\circ$ . The action of  $\text{HNO}_3$  upon Benary's "indigo" gives 3,5-dihydroxy-4-carbethoxy-2-nitrotyrrole, needles, decomp.  $100^\circ$ . The  $\text{FeCl}_3$  reaction is positive. The alk. solns. are pale red, the acid solns. colorless. *Potassium salt*, yellow, easily sol. in  $\text{H}_2\text{O}$  and decomps.  $167^\circ$ . *Barium salt*, yellowish red needles, decomps.  $165^\circ$ .  $\text{Pb}(\text{OAc})_2$  gives a reddish yellow ppt.;  $\text{CuSO}_4$  gives no ppt. but addn. of a trace of  $\text{NH}_3$  produces a

voluminous green ppt. The color of the red alc. alk. soln. is discharged by  $H_2S$ , with the formation of a S-contg. compd., m.  $121^\circ$ . Sapon. of the ester gives 3,5-dihydroxy-2-nitropyrrolecarboxylic acid, needles, decomp.  $124^\circ$ . Ammonium salt, yellow, sol. in  $H_2O$  with a red color. Silver salt, dark red. Methyl ester, needles, decomp.  $112^\circ$ .  $CH_2N_2$  converts the Et ester into 5-hydroxy-3-methoxy-2-nitro-4-carbethoxypyrrole, pale yellow liquid, b.  $146^\circ$  and solidifies in a cooling mixt. The free acid forms needles and gives colorless ammonium and silver salts. 5-Hydroxy-3-methoxy-2-nitro-4-carbomethoxypyrrole, b.  $145^\circ$ . 5-Methyl-2-nitro-3-hydroxy-4-carbethoxypyrrole, needles, decomp.  $100.5^\circ$ . The free acid needles, decomp.  $124^\circ$ . The alk. soln. is dark red.  $CH_2N_2$  gives the 3-methoxy derivative, which did not crystallize, and which gave yellow alk. solns.

C. J. W.

Indigo group. II. A new vat dye from indigo and malonic ester. THEODOR POSNER AND GOTTFRIED PYL. Ber. 56B, 31-44(1923); cf. C. A. 15, 1024; Ger. pat. 281,998.—Ethyl indigomalonate (I) is best prepd. by adding 20.8 g. indigo to 800 cc. boiling  $PhNO_2$  and then adding 57.6 g.  $CH_2(CO_2Et)_2$  and 0.1 g. NaOH and boiling the mixt. for 6 hrs. It forms red-violet crystals with a Cu luster, m.  $296-7^\circ$ . Soly. in AcOH, 2.85%. The concd.  $H_2SO_4$  soln. is brownish red, from which  $H_2O$  ppts. it unchanged. The alc. alk. soln. is emerald-green. The potassium salt ppts. from an alc. soln. upon addn. of 50% KOH as an emerald-green powder, from which I can be recovered by acidification. Continued heating with KOH gives products the N content of which depends upon the time of heating. I may be condensed with  $PhCH_2COCl$ , giving ethyl anhydro[phenylacetic acid]-indigomalonate (II), brick-red crystals, m. above  $310^\circ$ . The  $C_6H_4Me_2$  soln. shows a green fluorescence while the concd.  $H_2SO_4$  soln. is brownish red.



Ethyl benzoyl[dihydroindigomalonate], prepd. by reducing I and then condensing with  $BzCl$ , leaflets, turns red about  $192^\circ$  and decomp. without melting at higher temps. Ethyl benzoyl[indigomalonate] is best prepd. by heating I in  $C_6H_5N$  with  $BzCl$ , orange leaflets, m.  $240^\circ$ . Solns. in hydrocarbon solvents have a green fluorescence. Acetyl derivative of I, red, m.  $182^\circ$ . Nitroso derivative, brick-red crystals, decomp.  $267-70^\circ$ . Heated in AcOH with Zn, a bluish red soln. 1st results, which is then decolorized. The compd. is not changed by boiling 3 hrs. with  $Ac_2O-AcCl$ .  $BzCl$  in  $C_6H_5N$  gives the benzoylnitroso derivative, orange-yellow, sublimes about  $236^\circ$ , decomp.  $245-50^\circ$ . KOH in EtOH regenerated the NO deriv. A by-product of the NO deriv. is a compound,  $C_{21}H_{17}O_7N_3$ , needles, which turn red at  $210^\circ$ .

C. J. WEST

1-Alkyl-3-chloropyrazoles and 1-alkyl-3-pyrazolones. C. A. ROJAHN. Ber. 55B, 2959-71(1922).—R. attempted to prep. 1-alkyl-3-methyl-5-chloropyrazoles from  $NaN.CCl:CH.CMe:N$  (A) (C. A. 4, 2826) by treating it with alkyl halides, according to the equation  $A + MeI = \underline{NMe.CCl:CH.CMe:N} + NaI$  but the reaction

did not proceed in the manner expected. Either the alkyl radical migrated from the 1- to the 2-position or A is attacked at the N in the 2-position and the NaI splits off and instead of  $MeN.CCl:CH.CMe:N$  there is formed  $MeN.N:C(Cl)CH.CMe$ . The chloropyrazoles obtained through the Na salt are alkali-insol. so that the isomeric compds. unsubstituted in the 1-position are impossible. The compds. prepd. from A react readily with Br and  $HNO_3$  and this indicates a H atom in the 4-position. The corresponding

Ph deriv. of A was treated as was A in the hope that the compds. secured might be compared with 1-methyl-5-phenyl-3-chloropyrazole, m. 76°, or 1-methyl-3-phenyl-5-chloropyrazole, m. 82°. The compd. m. 43°. The methylation of phenylchloropyrazole is hardly comparable with that of A since the Na salt of the former is insol. in ether and alc. had to be used. To secure 1-alkylchloropyrazoles by a different method, 3-methyl- and 3-phenyl-5-pyrazolones were methylated and these compds. when treated with  $\text{POCl}_3$  gave a product identical with that obtained from A. 10 g. 3-Methyl-5-chloropyrazole (A') in 50 cc. abs.  $\text{Et}_2\text{O}$  and 2.25 g. Na wire were warmed 5 hrs. on a water bath and then heated in bomb tubes with 13.5 g. MeI for 12 hrs. in a water bath. NaI sepd. at once and after heating, a yellow  $\text{Et}_2\text{O}$  soln. with an odor resembling  $\text{C}_6\text{H}_5\text{N}$  was filtered from the NaI. After removing the  $\text{Et}_2\text{O}$  8 g. 1,5-dimethyl-3-chloropyrazole (B) were obtained, tabular crystals from  $\text{H}_2\text{O}$ , m. 45–7° (yield 70%), sol. in  $\text{Et}_2\text{O}$ , alc.,  $\text{Me}_2\text{CO}$ , HOAc and  $\text{C}_6\text{H}_6$ , difficultly sol. in cold  $\text{H}_2\text{O}$ . It is stable at 208–10°, b<sub>m</sub> 138° and is volatile in steam, has an odor resembling  $\text{C}_6\text{H}_5\text{N}$  and a sweet burning peppermint taste. B was also prepd. by refluxing the Na salt of chloropyrazole with *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{Me}$  in  $\text{Et}_2\text{O}$ . The *p*- $\text{C}_6\text{H}_4\text{SO}_3\text{Na}$  is filtered off and washed with  $\text{Et}_2\text{O}$  and the  $\text{Et}_2\text{O}$  soln. when dried is distd. 1,3-Dimethyl-5-chloropyrazole is formed simultaneously (Michaelis and Hadanch, C. A. 1, 1852). 8 g. B in 15 cc. 25% HCl was treated in the cold with 0.75 g.  $\text{KNO}_3$  in 5 cc.  $\text{H}_2\text{O}$ . The yellow mixt. turned greenish and after standing in the cold green needles of the 4-nitroso derivative of B, m. 87°, sepd. One g. B in glacial HOAc was treated with 0.61 g. Br in 5 cc. glacial HOAc. After 0.5 hr.  $\text{H}_2\text{O}$  was added and an oil sepd. which soon solidified. 1,5-Dimethyl-4-bromo-3-chloropyrazole, long needles from alc., m. 56°. 1 g. B was heated with 2 g.  $\text{Me}_2\text{SO}_4$  over a free flame, and then the cooled mass was poured into  $\text{H}_2\text{O}$ . The  $\text{Me}_2\text{SO}_4$  in excess was decompd. by boiling on the water bath. Treatment with KI followed,  $\text{NaHCO}_3$  was added, then a few drops of bisulfate soln. The product was dried, extd. with abs. alc. filtered and when cold anhyd.  $\text{Et}_2\text{O}$  was added, colorless crystals of 1,5-dimethyl-3-chloropyrazole 2-methiodide, decomp. 184°, were formed (Michaelis and Lachwitz, C. A. 4, 2826). 10 g. A' in 100 cc. anhyd.  $\text{Et}_2\text{O}$  with 2 g. Na wire were allowed to interact and then the mixt. was treated with 14.5 g. EtI for 12 hrs. in bomb tubes on the water bath. After removing the solvent, an almost colorless oil remained which volatilized in steam and had the odor of  $\text{C}_6\text{H}_5\text{N}$ ; 1-ethyl-5-methyl-3-chloropyrazole, b. 216–8°, was formed. It is mobile at –17° and yielded 1-ethyl-4-bromo-5-methyl-3-chloropyrazole, m. 39°, when treated with Br. When 13 g. A' in  $\text{Et}_2\text{O}$  with 2.4 g. Na were allowed to interact and the product thus formed was treated with 13 g.  $\text{PhCH}_2\text{Cl}$  in bomb tubes for 12 hrs. at 100° NaCl sepd. This was filtered and the filtrate was shaken with 20 cc. of 3% KOH to sep. unchanged A', and then the  $\text{Et}_2\text{O}$  soln. was washed with  $\text{H}_2\text{O}$  and dried with  $\text{CaCl}_2$ . The soln. on evapn. gave a light yellow oil b. 295–300°, 1-benzyl-5-methyl-3-chloropyrazole, identical with the 1-benzyl-3-methyl-5-chloropyrazole of Michaelis and Bose (*Diss. Rostock, 1909*). 3,5,7-3-phenyl-5-chloropyrazole, m. 142° (Michaelis and Rassmanu, C. A. 1, 1852), in 50 cc. MeOH with 1.2 g. Na were treated with 0.75 g. *p*- $\text{C}_6\text{H}_4\text{SO}_3\text{Me}$  under a reflux for 10 hrs. After the alc. was distd. the residue was extd. with  $\text{Et}_2\text{O}$  and from the ext. an almost colorless oil, methylphenylchloropyrazole, m. 43°, b. 295–7°, was obtained. This compd. in glacial HOAc was treated with Br and then the mixt. was treated with  $\text{H}_2\text{O}$ . The oil which sepd. solidified readily, needles from alc., m. 67°, 1-methyl-2-phenyl-4-bromo-2-chloropyrazole. It possibly is identical with 1-methyl-3-phenyl-4-bromo-5-chloropyrazole, m. 65° (C. A. 1, 1852). 15 g. 3,4-dimethyl-5-pyrazolone (v. Rothenburg, *J. prakt. Chem.* [2] 52, 40(1895)), m. 269° (and not 249°), were treated with 30 g.  $\text{POCl}_3$  for 12 hrs. in bomb tubes at 140–50° and then the mixt. was poured into ice water and neutralized carefully with  $\text{Na}_2\text{CO}_3$ . 3,4-Dimethyl-5-chloropyrazole (C) sepd. as a white powder ( $\text{Et}_2\text{O}$  was used to ext. the aq. soln.), long needles from hot  $\text{H}_2\text{O}$  or petr. ether, m. 124–5°,

b. 251-2°, volatile in steam and gives no compds. with Br. It yields *1-benzoyl-3,4-dimethyl-5-chloropyrazole* (Schotten-Baumann method), silky needles, m. 90-1°, from dil. alc., easily sol. in Et<sub>2</sub>O, alc. and C<sub>6</sub>H<sub>6</sub> and with hot H<sub>2</sub>O it gives C. When 5 g. B were heated with 10 cc. EtBr in bomb tubes for 12 hrs. at 180-200° *1-ethyl-5-methyl-3-chloropyrazole methobromide* was formed, thick crystals m. 225°. This compd. when heated loses EtBr, and *1-ethyl-5-methyl-3-chloropyrazole* is formed, b. 215-20°, colorless non-cryst. product having the odor of C<sub>6</sub>H<sub>5</sub>N. 5 g. 3-methyl-5-pyrazolone (D), m. 220° (cf. Michaelis and Lachwitz, *C. A.* 4, 2826), were heated at 100° with 24 cc. of NaOMe soln. contg. 5 g. Na in 100 cc. alc. and 6 g. MeI in bomb tubes for 12 hrs. The alc. was distd. off and the residue in CHCl<sub>3</sub> gave after evapn. a brown oil from which crystals sepd. after a few days. *1,5-Dimethyl-3-pyrazolone* (E),  $\text{MeN.CMe:CH.C(OH):N}$  or  $\text{MeN.CMe:CH.CO.NH}$ . m. 172-3° (*Ber.* 39, 3267(1906)). The oil was 1-methylanti-

pyrine. 9.81 g. D with 2.3 g. Na in 60 cc. MeOH were heated 6 hrs. with 18.62 g. *p*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Me in 50 cc. MeOH. The cryst. mass was sucked dry, and washed with CHCl<sub>3</sub>. The CHCl<sub>3</sub> soln. yielded 3.5 g. of a dimethylpyrazolone, m. 181-2° (F), and about 4 g. 1-methylanti-pyrene. 1 g. E in 5 cc. glacial HOAc was treated dropwise with Bf until an excess was present, and after 1 hr. H<sub>2</sub>O was added and crystals of *1,5-dimethyl-4-bromo-3-pyrazolone* were thrown out, colorless needles, m. 209°, from dil. HOAc. F gave on bromination a bromide m. 218°. The mixt. of the 2 bromides m. 210°. 10.0 g. D in 20 cc. abs. alc. and 2.85 g. Na in 48 cc. abs. alc. were heated 24 hrs. in bomb tubes with 15.73 g. EtI. The alc. was then distd. and the residue was extd. with Et<sub>2</sub>O. The residue from Et<sub>2</sub>O when crystd. from hot H<sub>2</sub>O gave colorless needles of *1-ethyl-5-methyl-3-pyrazolone*, m. 135-6°. It gave a bromide m. 39°. 16 g. 3-phenyl-5-pyrazolone, m. 236°, from BzCH<sub>2</sub>CO<sub>2</sub>Et and N<sub>3</sub>H<sub>4</sub>, were treated with 2.3 g. Na in 100 cc. MeOH, and then 18.62 g. *p*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Me in MeOH were refluxed with the mixt. for 5 hrs. *p*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na was removed by filtering and the procedure was then identical with that used in the case of E. The colorless oil, b<sub>60</sub> 230-45°, solidified to colorless crystals of 1-methylphenylpyrazolone (G), m. 165°, recrystd. from H<sub>2</sub>O. 1-Methyl-3-phenyl-5-pyrazolone, m. 207° (Michaelis and Hadanck). A *methylphenylpyrazolone* (H), m. 96°, was also prepd. in small amts. G heated with POCl<sub>3</sub> in bomb tubes at 210° gave the chloropyrazole m. 62-3° to which Michaelis gave the constitution 1-methyl-3-phenyl-5-chloropyrazole. H gave resins when treated with this reagent. 5.0 g. E was heated 12 hrs. with 8 cc. POCl<sub>3</sub> at 200-10°, the product was then treated with ice water, neutralized with Na<sub>2</sub>CO<sub>3</sub> and 1,5-dimethyl-3-chloropyrazole was steam-distd. The distillate had an odor of C<sub>6</sub>H<sub>5</sub>N. The distillate was extd. with Et<sub>2</sub>O and the residue from the Et<sub>2</sub>O when crystd. from hot H<sub>2</sub>O gave tabular crystals m. 46-7°. The mixt. of this product and B m. 46-7°.

II. F. WILLIAMS

**Stereochemical investigations of the diketothiazolidines.** I. STEN KALLÉNBERG. *Ber.* 56B, 316-31(1923).—EtNHCOSK may be prepd. by treating KOH in abs. EtOH with EtNH<sub>2</sub>.HCl, filtering off the KCl and passing through the filtrate a stream of COS; the crude product obtained by evapn. *in vacuo* over H<sub>2</sub>SO<sub>4</sub> is ready for use. *d*-N-Ethyl-carbamictiomatic acid (A), (EtNHCOS)CH(CO<sub>2</sub>H)CH<sub>2</sub>CO<sub>2</sub>H, from 1-HO<sub>2</sub>CCHBr-CH<sub>2</sub>CO<sub>2</sub>H in Na<sub>2</sub>CO<sub>3</sub> and EtNHCOSK by standing 48 hrs. at 0°; repeated crystn. from AcOH gave a product, m. 134-5°,  $[\alpha]_D$  103.5°,  $[M]$  228.9°. If the reaction is carried out at higher temp. a large amt. of *dl*-acid results. Concd. NH<sub>4</sub>OH decomps. A at room temp., giving among other products *d*-thiomalic acid (B). Acids or alkalis decomp. A with the formation of B, CO<sub>2</sub> and EtNH<sub>2</sub>. The *dl*-acid forms small thin prisms, or short needles, m. 141-2°. When A is allowed to stand with concd. HCl for 6 weeks, the *dl*-form of *N*-ethyldiketothiazolidineacetic acid results, flat prisms, m. 113-5°. After 48 hrs., a sirupy product is obtained which is the *d*-acid with  $[\alpha]_D$  of 169.2°. This is

inactivated by NaOH. In the hope of obtaining a cryst. *d*-acid, the *dl*-form was combined with *l*-MeCH<sub>2</sub>PhNH<sub>2</sub>; the double salt forms small needles, m. 135–7°, but upon decompn. with H<sub>2</sub>SO<sub>4</sub> gave only the sirupy active acid, *d*-*N*-methylcarbamichthiomalic acid, m. 114–6° (decompn.), [α]<sub>D</sub> 99.2°. The *dl*-acid (C) forms small spherical aggregates, m. 135–6° (decompn.). *d*-*N*-Methyldiketothiazolidineacetic acid, long transparent prisms, m. 101–2°, [α]<sub>D</sub> 208°. This is transformed into the *dl*-form by alkali, also obtained by treating C with concd. HCl, small plates, m. 98–9°. *d*-*N*-Dimethylcarbamichthiomalic acid, small prisms, m. 138–9°, [α]<sub>D</sub> 81.7°. This acid is not decompd. by concd. NH<sub>4</sub>OH at room temp., but is decompd. by heating with *N* NaOH or H<sub>2</sub>SO<sub>4</sub>.

C. J. WEST

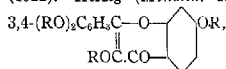
**Stereochemical studies. VII. 4-Methyl-2-thiothiazoline-3-acetic acid.** BERTIL GROTH AND BROR HOLMBERG. *Ber.* 56B, 289–98(1923); cf. *C. A.* 16, 2116.—*4*-Methyl-2-thiothiazoline-3-acetic acid (A) (thiko is used for thio-keto), C<sub>6</sub>H<sub>7</sub>O<sub>2</sub>S<sub>2</sub>N, is prepd. by treating 12 g. H<sub>2</sub>NCH<sub>2</sub>CO<sub>2</sub>H·HCl with 19 g. KOH in 50 cc. H<sub>2</sub>O and stirring with 8 g. CS<sub>2</sub> for several hrs. (soln. of the CS<sub>2</sub>) and then shaking the cooled mixt. with 9 g. ClCH<sub>2</sub>Ac, pale honey-yellow compact plates or short prisms, m. 198–9° (decompn.). *Sodium salt*, with 5H<sub>2</sub>O, small rectangular plates. *Barium salt*, rosetts of thin, glistening needles, contg. 2H<sub>2</sub>O. *Methyl ester*, long needles, m. 96–7°. *Ethyl ester*, cm.-long needles, m. 97–8°. *1-Phenylethylamine salt*, grayish green needle-like prisms, m. 161–2°. *d*-Phenylethylamine salt, m. 160–2°. No resolution was secured in either case. The only reaction product from the oxidation of A with HNO<sub>3</sub> was an inner anhydride of 4-methyl-2-hydroxythiazoline-3-acetic acid,

$$\begin{array}{c} \text{CH}_2 \text{---} \text{N} \text{---} \text{CMe} \\ | \quad \quad | \\ \text{CO} \text{---} \text{O} \text{---} \text{CH} \text{---} \text{S} \text{---} \text{CH} \end{array}$$
, isolated as the acid sulfate,

cryst. powder, somewhat hygroscopic, and m. 114–5°. Although the anhydride easily reacts with alkali, it is impossible to isolate any salts. The *chloride* results by the action of BaCl<sub>2</sub> upon the sulfate, and crystallizes with 1 H<sub>2</sub>O as large flat prisms, which m., when anhyd., about 230°. The *free base* was prepd. from the sulfate by quant. removing the H<sub>2</sub>SO<sub>4</sub> with Ba(OH)<sub>2</sub>, flat prisms, m. 165° (decompn.). The free base is much more unstable than the salts.

C. J. WEST

**Synthesis of fisetol.** ADOLF SONN AND SUSANNE FALKENHEIM. *Ber.* 55B, 2975–85 (1922).—Herzig (*Monatsh.* 12, 184(1891)) heated tetraalkyl ethers of "fisetin,"



with alc. KOH and obtained in addn. to dialkylproto-

catechuic acid derivs., a compd. C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>, the structure of which he gave as ω-hydroxyresacetophenone, 2,4-(HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCH<sub>2</sub>OH, calling it fisetol (A). He could not obtain A by removing the alkyl groups from the ether. Synthesis failed him. Tambor and Dubois (*C. A.* 13, 448) converted 2,4-HO(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCH<sub>2</sub>Br by treatment with Ac<sub>2</sub>O and NaOAc into the Br-free diacetate and when this compd. was treated with alc. KOH the 4-Me ether of A was obtained. There is no mention made of attempts to remove the Me groups. S. and F. could not find this ether when 2,4-HO(EtO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCH<sub>2</sub>Cl was treated with Ac<sub>2</sub>O and NaOAc, but they did find acetyl-5-methoxycoumaranone. When 2,4-(HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCH<sub>2</sub>Br was treated with Ac<sub>2</sub>O and NaOAc, 5-hydroxycoumaranone diacetate and a Br-free compd., m. 118° after several crystns. from MeOH, were formed. The compd. which resulted when this product was treated for the removal of the Ac group m. 257°, and was probably a condensation product formed from 2 mols. of (HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCH<sub>2</sub>Br. (HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCH<sub>2</sub>I and its di-Ac deriv. were rubbed with Ag<sub>2</sub>O and also with AgNO<sub>3</sub>. In both cases 5-hydroxycoumaranone was formed. Attempts to produce A by diazotizing (HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>COCH<sub>2</sub>NH<sub>2</sub> failed. When C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> was treated with AcOCH<sub>2</sub>CN the expt. was a failure but succeeded with carbethoxy- and carbomethoxyglycolic nitrile. *m*-C<sub>6</sub>H<sub>4</sub>-



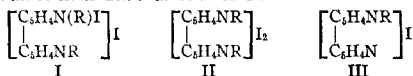
$(\text{OH})_2 + \text{NCCH}_2\text{OCO}_2\text{Et} \longrightarrow 2,4-(\text{HO})_2\text{C}_6\text{H}_3\text{C}(\text{:NH}\cdot\text{HCl})\text{CH}_2\text{OCO}_2\text{Et}$ . Hydrolysis of the ester led to A. 1 g. methoxycoumaranone and 1 g. freshly melted NaOAc with 10 cc.  $\text{Ac}_2\text{O}$  were refluxed 3 hrs. When the reaction product was poured into  $\text{H}_2\text{O}$  a brown oil sepd. which soon solidified. When crystd. after treatment of the alc. soln. with bone black the *O*-acetyl-5-methoxy(enol)coumaranone, m.  $62^\circ$ , sepd. in pearly crystals, easily sol. in  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ , ligroin, and  $\text{CHCl}_3$ .  $\text{H}_2\text{O}$  throws them out of alc.  $\text{Me}_2\text{CO}$  and glacial HOAc. 1 g.  $\text{BrCH}_2\text{CN}$  and 1.2 g. *m*- $\text{C}_6\text{H}_4(\text{OME})_2$  in 3 cc. anhyd.  $\text{Et}_2\text{O}$  were mixed with 1.2 g. freshly ignited  $\text{ZnCl}_2$  and treated with dry HBr. The lower layer solidified on standing overnight. The  $\text{Et}_2\text{O}$  was poured off, the residue was shaken with  $\text{Et}_2\text{O}$  and then heated to boiling with  $\text{H}_2\text{O}$  for 15 min. The molten mass soon solidified, and when crystd. from alc. yielded the  $\omega$ -bromoacetoresorcinol dimethyl ether, m.  $101-2^\circ$ , white crystals, easily sol. in  $\text{Et}_2\text{O}$ , alc. and  $\text{C}_6\text{H}_6$ .  $\text{Et}_2\text{O}$  and ligroin dissolve only small amts. 5 g. resorcinol and 5 g.  $\text{BrCH}_2\text{CN}$  in 20 cc.  $\text{Et}_2\text{O}$  were satd. with HBr after 5 g.  $\text{ZnCl}_2$  were added. The reaction mixt. was oily and after standing overnight did not crystallize. The imide hydrochloride (bromide?) was decompd. by boiling with  $\text{H}_2\text{O}$ .  $\omega$ -Bromoacetoresorcinol (A') m.  $127^\circ$ , easily sol. in alc. and  $\text{Me}_2\text{CO}$ . Ligroin ppts. it from  $\text{Et}_2\text{O}$ . It seps. from hot HOAc and  $\text{C}_6\text{H}_6$  in thick crystal clusters and the alc. soln. gives a Bordeaux-red color with  $\text{FeCl}_3$ . The diacetate was formed when 1 g. A' with 2 g.  $\text{Ac}_2\text{O}$  was treated with 1 drop  $\text{H}_2\text{SO}_4$ . The mixt. poured into  $\text{H}_2\text{O}$  gave a yellow greenish oil which soon solidified, yielding square prisms, m.  $76^\circ$ , sol. in HOAc,  $\text{EtOAc}$  and  $\text{C}_6\text{H}_6$ . 6.9 g. 2,4-(HO) $_2\text{C}_6\text{H}_3\text{COCH}_2\text{Cl}$  (C. A. 4, 2441) in  $\text{Me}_2\text{CO}$  were treated with 8 g. NaI in  $\text{Me}_2\text{CO}$ . NaCl sepd., the mixt. standing overnight. When  $\text{H}_2\text{O}$  was added to the mixt. the emulsion which formed soon yielded long white needles of  $\omega$ -iodoacetoresorcinol (B), m.  $141^\circ$ , long flat prisms, easily sol. in  $\text{Et}_2\text{O}$ , alc.,  $\text{Me}_2\text{CO}$  and HOAc, insol. in ligroin and  $\text{CHCl}_3$ . The diacetate was obtained by treating 2 g. B with  $\text{Ac}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ . The mixt. became clear on warming and when  $\text{H}_2\text{O}$  was added to the mixt., an oil sepd. which soon became an amorphous mass, thick prisms, m.  $97^\circ$ ; this product was also formed by treating  $(\text{AcO})_2\text{C}_6\text{H}_3\text{COCH}_2\text{Cl}$  with NaI, sol. in HOAc,  $\text{Me}_2\text{CO}$ ,  $\text{C}_6\text{H}_6$  and  $\text{CHCl}_3$ .  $\omega$ -Iodoacetoresorcinol 2-methyl ether was prepd. like the Me-free compd. It is easily sol. in hot HOAc,  $\text{EtOAc}$ ,  $\text{Me}_2\text{CO}$ , and alc., crystg. in needles, m.  $128^\circ$ , sol. in hot  $\text{C}_6\text{H}_6$ , more difficultly in  $\text{CHCl}_3$ , insol. in  $\text{Et}_2\text{O}$  and ligroin. The alc. soln. gave a red color with  $\text{FeCl}_3$ . 5 g.  $\text{ClCH}_2\text{CN}$  were heated at  $140^\circ$  with  $\text{C}_6\text{H}_4(\text{CO})_2\text{NK}$  for 2 hrs. in a  $\text{C}_6\text{H}_4\text{Me}_2$  bath. The dark brown mass was cooled, and rubbed with considerable  $\text{H}_2\text{O}$  to remove excess  $\text{C}_6\text{H}_4(\text{CO})_2\text{NK}$  and the insol. phthalimidoacetoneitrile was crystd. from dil. HOAc, colorless thin flakes, m.  $124-5^\circ$ , sol. in alc.,  $\text{Me}_2\text{CO}$ , HOAc,  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_4\text{Me}_2$  and difficultly sol. in  $\text{Et}_2\text{O}$  and ligroin. 10 g. resorcinol in 40 cc. anhyd.  $\text{Et}_2\text{O}$  were treated with 8 g. freshly melted  $\text{ZnCl}_2$  and 8.8 g. hippuryl cyanide. Dry HCl was passed into the mixt. and an oil sepd. which after removal of the  $\text{Et}_2\text{O}$  was washed with 100 cc.  $\text{H}_2\text{O}$ . After heating for a few min.  $\omega$ -benzoylaminoresacetophenone sepd., m.  $252^\circ$ , difficultly sol. in hot alc. and almost insol. in  $\text{H}_2\text{O}$ ,  $\text{EtOAc}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{Et}_2\text{O}$  and ligroin. To 1.5 g. resorcinol and 1.3 g.  $\text{EtO}_2\text{CNHCH}_2\text{CN}$  in 12 cc. dry  $\text{Et}_2\text{O}$  were added 1.5 g. freshly melted  $\text{ZnCl}_2$  and the mixt. was satd. with HCl. An oil soon sepd. from the red soln. The  $\text{Et}_2\text{O}$  was poured out, and the imide hydrochloride was decompd. by boiling with  $\text{H}_2\text{O}$ . On cooling  $\omega$ -[carbethoxyamino]acetoresorcinol sepd., crystals, m.  $156-7^\circ$ , from hot  $\text{H}_2\text{O}$ , easily sol. in hot HOAc,  $\text{AcOEt}$ ,  $\text{AcOH}$ , alc.,  $\text{Me}_2\text{CO}$ ,  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ , ligroin and  $\text{CHCl}_3$ . This product refluxed 2 hrs. with 40 parts HCl (1:1) gradually dissolved. About 0.5 of the material sepd. unchanged but when the filtrate was evapd.  $\omega$ -aminoresacetophenone was obtained, tables decomp.  $257^\circ$  (cf. Tutin, C. A. 5, 2853). 8 g.  $\text{HOCH}_2\text{CN}$  in 80 cc. dry  $\text{C}_6\text{H}_6$  were cooled and treated with 10 g.  $\text{PhNMe}_2$  and 10 g.  $\text{ClCO}_2\text{Et}$ . On shaking, the nitrile dissolved, giving a green mixt. 10 g.  $\text{PhNMe}_2$  and 10 g. ester were added after 20 min. and then again for a third time. On standing

2 hrs. in ice  $H_2O$  the  $PhNMe_2$  was sepd. by shaking the mixt. with  $HCl$ , followed by treatment with  $H_2O$ . The  $C_6H_6$  ext. dried over  $Na_2SO_4$  was distd. under reduced pressure. *O*-Carbomethoxyglycolic nitrile (C),  $b_{30}$   $127^\circ$ , is a colorless mobile liquid, having a peculiar odor; the compd. is colored red with  $H_2SO_4$ . *O*-Carbomethoxyglycolic nitrile (D),  $b_{48}$   $116-8^\circ$ , was prepd. in a similar manner. 5.5 g. resorcinol and 4.5 g. C in 20 cc.  $Et_2O$  with 5 g. freshly melted  $ZnCl_2$  were treated in the cold with dry  $HCl$ . The oily layer which sepd. was removed from the  $Et_2O$  layer and after washing several times with  $Et_2O$  the ketimide hydrochloride was decompd. by boiling with  $H_2O$ . The brown yellow oil which settled solidified to shiny flakes of  $\omega$ -carbomethoxyxyresacetophenone (E), m.  $104-5^\circ$  after drying over  $P_2O_5$ , rectangular shining white tables from  $HIOAc$ ,  $Me_2CO$  and alc. after  $H_2O$  is added to these solvents, sol. in  $Et_2O$ , hot  $C_6H_6$  and  $CHCl_3$ , insol. in ligroin. 4.2 g. D and 5.5 g. resorcinol gave 5.6 g.  $\omega$ -carbomethoxyxyresacetophenone (F), long white needles from  $H_2O$ , m.  $157-8^\circ$ , easily sol. in cold  $Me_2CO$  and  $EtOAc$ , in hot alc. and glacial  $HOAc$ , difficultly sol. in hot  $H_2O$  and almost insol. in  $Et_2O$ ,  $C_6H_6$ ,  $CHCl_3$  and ligroin. 1 g. E (or F) in 10 cc. 2 *N*  $NaOH$  was allowed to stand at room temp. 2 hrs. The yellow-greenish soln. which turned red was treated with 2 *N*  $HCl$ .  $CO_2$  was evolved and the oil which sepd. soon solidified.  $\omega$ -Hydroxyresacetophenone or fisetol was recrystd. from the alc. soln., and the crystals were dried at  $100^\circ$ ; prisms m.  $189^\circ$ , easily sol. in  $EtOAc$ ,  $Me_2CO$ , in hot  $H_2O$ , alc. and  $HOAc$ , insol. in  $Et_2O$ ,  $C_6H_6$  and ligroin. The alc. soln. with  $FeCl_3$  gave a Bordeaux-red color. It reduces  $NH_3-AgNO_3$  and alk.  $Cu$  soln. The phenylhydrazone m.  $109^\circ$  (decompn.), yellow needles from alc., easily sol. in  $Me_2CO$ ,  $EtOAc$ , and  $Et_2O$ , alc., and  $HOAc$ , almost insol. in hot  $H_2O$ ; ligroin ppts. it from hot  $C_6H_6$ . C when condensed with  $m-C_6H_4(OMe)_2$  in  $Et_2O$  gave  $\omega$ -[carbomethoxyxy]resacetophenone dimethyl ether, white rectangular tables, m.  $74-5^\circ$ , and when decompd. in  $Me_2CO$  with alkali and then acidified, yielded a brown oil  $O^4,O^4$ -dimethylfisetol. The phenylhydrazone m.  $212^\circ$ , pearly plates from alc.

H. L. WILLIAMS

The color of  $\gamma,\gamma'$ -dipyridylum halides. BRUNO EMMERT AND JULIUS STAWITZ. *Ber.* 56B, 83-91(1923).—The following derivs. of  $\gamma,\gamma'$ -dipyridyl are described: *Dihydroiodide*,  $C_{10}H_{10}N_2I_2$ , red prisms, sol. in 5 parts  $H_2O$  at room temp., and in boiling  $EtOH$  with a yellow color. The *hydroiodide hydrate*,  $C_{10}H_{10}N_2I \cdot H_2O$ , forms golden yellow prisms. The *dihydrobromide* forms long, yellowish needles, while the *hydrobromide* crystallizes with 1  $H_2O$  as colorless prismatic needles. The *hydrochloride* also contains 1 $H_2O$ . The *dimethiodide* is sol. in 10 parts  $H_2O$  at room temp.; the alc. soln. is yellowish red. The *methiodide*, which is formed at the same time, may be extd. with  $MeOH$  and forms a fine light yellow powder; its *hydroiodide* forms a light reddish brown powder. The *dimethobromide* forms yellow prisms. *Ethiodide*, yellow, glistening leaflets; the following extinction coeffs. were detd.: In aq. soln.,  $N/40$ ,  $\epsilon_{366}$  16.75°,  $\epsilon_{415}$  7.52;  $N/80$   $\epsilon_{366}$  11.66,  $\epsilon_{416}$  6.64; in  $EtOH$ ,  $N/250$ ,  $\epsilon_{358}$  171,  $\epsilon_{415}$  81.19,  $\epsilon_{438}$  35.83;  $N/500$ ,  $\epsilon_{359}$  137.2,  $\epsilon_{405}$  60.3,  $\epsilon_{436}$  28.68. The *diethiodide*, orange prisms, is sol. in 3 parts  $H_2O$  at room temp. The extinction coeffs. in aq. soln.:  $N/40$ ,  $\epsilon_{415}$  43.6;  $N/80$ ,  $\epsilon_{405}$  27.96. *Dipropiodide*, red; the concd. alc. soln. is red, becoming yellowish red on diln. In aq. soln.,  $N/40$ ,  $\epsilon_{435}$  16.07;  $N/80$ ,  $\epsilon_{438}$  10.31; in alc. soln.,  $N/1000$ ,  $\epsilon_{435}$  493.1,  $\epsilon_{436}$  498.7;  $N/2000$ ,  $\epsilon_{436}$  432.7,  $\epsilon_{438}$  354.6. In moist air the yellow *pentahydrate* is formed, which gradually loses its  $H_2O$ , forming the red anhyd. deriv. The *propiodide* is yellow and more easily sol. in  $CHCl_3$ . The *dipropobromide* is greenish yellow with a marked surface luster. The *dipropochloride* forms glistening leaflets. The *methiodide propiodide* is formed from the  $MeI$  deriv. by heating with  $PrI$  and forms red prisms. *Isobutiodide*, red. *Isoamyl iodide*, is somewhat darker than the *iso-Bul* deriv. The *di-sec-hexyl iodide derivative* was isolated as the *dihydrate*, yellow needles, which loses  $H_2O$  upon warming or in vacuum, forming the brownish red *iodide*. Heating with  $H_2O$  splits off  $C_6H_{12}$  and

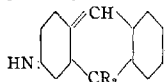
forms the di-HI deriv. *Dibenzyl iodide derivative*, isolated as the yellow *dihydrate*, is red. It dissolves in about 150 parts  $H_2O$  at  $20^\circ$ , forming a pale yellow soln. In hot alc. the color is a reddish yellow. The *dibenzyl bromide derivative* was isolated as the light yellow *tetrahydrate*. The red di-iodides are formulated as the pseudo form  $(IRNC_6H_5)_2$ , the yellow moniodides as  $NH_2C_6H_4C_6H_4NRI$ . The yellow hydrates are written as I. In  $H_2O$  and EtOH solns. the di-iodides occur as the red pseudo form, the mixed yellow form (I) and the colorless true salt form (II), the last two being dissociated. The variation from Beer's law in the solns. of the monoalkyl halides is explained by shifting of the equil. between II and the colorless mol. of the formula III.



C. J. WEST

The color of the di- and tri-2-quinolylmethanes and their derivatives. GÜNTHER SCHEIBE. *Ber.* 56B, 137-48(1923); cf. *C. A.* 16, 3110; 17, 762.—Addn. of 4 mols.  $HNO_3$  to alc.  $CH_2(C_6H_4N)_2$  causes the pptn. of the *dinitrate*, glistening leaflets. Upon heating or upon warming in EtOH 1 mol.  $H_2O$  is split off, giving the compd.  $C_{19}H_{17}O_2N_4$  (*nitrodi-2-quinolylmethane nitrate*), yellow plates, m.  $145^\circ$ . *Sodium salt*, yellow. From this salt, HCl ppts. the free *nitro compound*,  $C_{19}H_{17}O_2N_3$ , yellow needles, m.  $200^\circ$ . Excess  $HNO_3$  gives the above nitrate and HCl gives a *hydrochloride*.  $HNO_3$  added to an AcOH soln. gives the *dinitro compound*,  $C_{19}H_{17}O_4N_4$ , prisms, m.  $140^\circ$ . This is insol. in HCl or NaOH. *Tri-2-quinolylcarbinol acetate*, prisms, m.  $190^\circ$ . *Tri-2-quinolylmethane bromide*, m.  $169^\circ$ . In Et<sub>2</sub>O this forms a *dipicrate*. With EtOH-KOH the bromide forms the *ethyl ether*, m.  $179^\circ$ .  $PhNHNH_2$  smoothly reduces the bromide to the methane deriv. [*p*-*Dimethylaminobenzal*]*picoline*, by heating  $\alpha$ -picoline with *p*- $Me_2NC_6H_4CHO$  and  $ZnCl_2$ , pale yellow, m.  $139^\circ$ . With acids this yields colored salts, which are decomp. by alkali. The action of  $HNO_3$  upon an acid soln. gives a colored substance, stable towards alkali, which is probably a nitrosoamine. For purposes of comparison of absorption spectra,  $PhNH_2$  and  $AcCH_2Me$  were heated in alc. with  $ZnCl_2$ , giving *acetylacetone dianil-zinc chloride*, prisms, decomp.  $256^\circ$ . Decomp. with  $NH_3$ , this salt gives an oil which then decomp. into the monoanil and  $PhNH_2$ . The monoanil may be condensed with  $PhNH_2 \cdot HCl$  to form the *dianil hydrochloride*, yellow prisms, m.  $218^\circ$ . C. J. W.

Several anthracene derivatives. F. KEHRMANN, RAOUL MONNIER AND MARIE RAMM. *Ber.* 56B, 169-74(1923).—The prepn. of the carbazine dyes indicates the possibility of the existence of a new class of *p*-quinonimide dyes with the chromogen



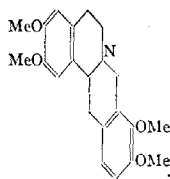
Thus far expts. looking towards the prepn. of such dyes

have failed. *9-Phenyl-10,10-diethyl-9,10-dihydro-9-anthranol* was obtained by the action of  $PhMgBr$  upon 10,10-diethyl-9-anthrone, needles, m.  $111-2^\circ$ . The concd.  $H_2SO_4$  soln. is yellow and has a green fluorescence; concd.  $HClO_4$  is colored orange and concd.  $HNO_3$  a yellowish red. The concd.  $H_2SO_4$  soln., upon treatment with EtOH, yields the corresponding *anthracene derivative*, needles, m.  $135-6^\circ$ ; the EtOH soln. has a marked blue fluorescence. Diethylanthrone, reduced with Zn in AcOH, gives *9,9-diethyl-9,10-dihydroanthracene*, fine needles, m.  $210^\circ$ . Attempts to nitrate 9,10,10-triphenyl-9,10-dihydro-9-anthranol were not successful. Expts. in which 9,10-diphenyl-9,10-dihydro-9,10-dianthranol was dissolved in concd.  $H_2SO_4$  showed that decompn. occurred with the formation of anthraquinone, 9,10-diphenylantracene and an intensely orange-yellow compd., not yet obtained pure. C. J. WEST

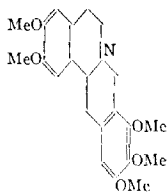
Remarks upon the article of Kurt Hess and Ottmar Wahl: "The constitution

of scopolamine and scopoline. The Hoffman decomposition of scopoline." J. GADAMER. *Ber.* 56B 130-1(1923).—Polemical. Cf. Hess, *C. A.* 17, 397. C. J. WEST

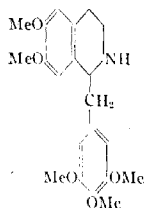
Constitution of the alkaloids of colombo root. ERNST SPÄTH AND KARL BÖHM. *Ber.* 55B, 2985-95(1922).—S. and Lang (*C. A.* 16, 1778) showed that the methylenedioxy group of berberine when substituted by 2 MeO groups gave a base identical with palmatine (I). Gunzel (*Arch. Pharm.* 244, 257(1906)) found columbamine (AA),



I



II



III

$C_{21}H_{22}NO_3OH$ , and Feist (*C. A.* 2, 1141) isolated jatrorrhizine (BB),  $C_{20}H_{20}NO_3OH$ , and concluded that AA and BB contain a phenolic group and by methylation were found to give the same product from which II was obtained. In AA Feist found 4 MeO groups and 1 OH group, and in BB there are 3 MeO and 2 HO groups. S. and B. attempted to synthesize II. From homoveratrylamine (A) and homogallic acid tri-Me ether (B) the corresponding acid amide was prepd. and from that the dihydroisoquinoline deriv. which by reduction gave III. Up to this point no difficulties were encountered, but when III was treated with methylal and HCl (Pictet and Gams, *C. A.* 6, 484) high melting and high mol. compds. were formed. B was prepd. by condensing gallic aldehyde tri-Me ether (*Ber.* 38, 3636(1905)) with hippuric acid, then splitting the azolactone and then oxidizing; and A (Rosenmund, *C. A.* 5, 893) was prepd. by condensing veratric aldehyde with  $MeNO_2$  followed by reduction of the  $\omega$ -nitrostyrene. 4.92 g. well dried B and 4.33 g. A were heated to  $175^\circ$  for 5 hrs. and the product in  $C_6H_6$  was washed with KOH and then with HCl. The residue from  $C_6H_6$  was a colorless oil, which soon crystd., white needles, trimethylhomogalloylhomoveratrylamine (C), m.  $98^\circ$ . The dihydroisoquinoline derivative (D) was prepd. by heating 5.9 g. well dried C in 150 cc. anhyd.  $C_7H_8$  to boiling and adding 24.5 g.  $P_2O_5$  during 20 min. The  $C_7H_8$  was poured out and the mass clinging to the walls of the vessel was treated with  $H_2O$  to dissolve it and shaken several times with  $Et_2O$ . The base set free with KOH was obtained from  $Et_2O$  as an amorphous glassy mass. The picrate, yellow crystals from hot alc., m.  $154-5^\circ$ . 4 g. D with Sn and 22 cc.  $H_2O$ , 44 cc. concd. HCl and 44 cc. alc. (to prevent sepn. of Sn double compds.) were refluxed. The reaction product was treated with  $H_2O$ , then with  $H_2S$  to remove Sn and the clear filtrate was evapd. at a low temp. *in vacuo* to a small vol. On treatment with alkali and shaking with  $Et_2O$  1,2,3,4-tetrahydro-6,7-dimethoxy-1-[trimethylgalloyl]isoquinoline (E) was formed, amorphous product. To characterize E as a sec. amine, the *N*-*m*-nitrobenzoyl derivative was prepd. (amorphous). The hydrochloride is difficultly sol. in HCl, white needles, sol. in  $H_2O$  and it may be prepd. by addn. of HCl to the  $H_2O$  soln. 0.498 g. E was refluxed in 30 cc. HCl and during 1 hr. 20 times the theoretical amt. of  $H_3C(OMe)_2$  was added. The mixt. was then made alk. and extd. with  $Et_2O$ . The white cryst. product m.  $292^\circ$  (decompn.), is difficultly sol. in alc. and  $Et_2O$  and a mol. wt. detn. showed that probably 2 mols. of E were condensed. The product is a true tetrahydroberberine deriv.; 1 g. was heated with 2 g. I and 4.5 cc. alc. for 2.5 hrs. in a bomb tube and the periodide formed was then decompd. with  $NaHSO_3$  and  $Na_2CO_3$ . The resulting iodide was decompd. in  $H_2O$  with KOH and the tertiary base

thus liberated was extd. with  $\text{Et}_2\text{O}$ . The quaternary iodide remained unattacked in  $\text{H}_2\text{O}$  and was pptd. by  $\text{KI}$ , and dil.  $\text{HCl}$  as a brown mass. This berberinium compd. when reduced with  $\text{Zn}$  and  $\text{HOAc}$  gave **E**. The other product formed in conjunction with the dimol. compd. was an amorphous monomol. product of the structure of a tetrahydroberberine, since on oxidation with **I** it gave a quaternary iodide. When 1 mol. of **E** and 1 mol. of  $\text{H}_2\text{C}(\text{OMe})_2$  were allowed to interact a berberinium iodide was formed. An amorphous tertiary base resulted when this product was reduced with  $\text{Zn}$  and  $\text{HOAc}$ . No well crystd. product m.  $148^\circ$  (Feist) was obtained. In isolating the alkaloids from colombo root, 4 kg. were extd. with alc. The ext. free of alc. was warmed with 6 parts  $\text{H}_2\text{O}$  and the cold soln. when treated with excess of  $\text{KI}$  deposited iodides, although part remained in colloidal condition. The mixt. stood 10 days in a tall cylinder and the iodides sepd. The aq. portion was removed, the sediment was heated with  $\text{H}_2\text{O}$  and  $\text{KI}$  when again added caused pptn. The crude alkaloids were treated with 10%  $\text{K}_2\text{CO}_3$  on the filter as long as the filtrate was brown, then 5%  $\text{KOH}$  was drawn through the mass, until the filtrate was colorless. The palmatine iodide remaining on the filter was dissolved in hot  $\text{H}_2\text{O}$ , filtered and pptd. with  $\text{KI}$ . Traces of phenolic bases were removed by treatment with cold dil.  $\text{KOH}$ . The iodide sol. in  $\text{K}_2\text{CO}_3$  was pptd. with  $\text{HCl}$  and  $\text{KI}$ . Thus the iodides were sepd. into a  $\text{KOH}$ -sol. and a  $\text{K}_2\text{CO}_3$ -sol. product. 4 kg. fresh root gave 13.2 g. palmatine iodide and 17 g. alkali-sol. iodides (**G**) and 25 g. carbonate-sol. iodides (**H**). Old root gave 5 g. palmatine, 8.5 g. **G** and 2.5 g. **H** iodides. 2 g. **H** in 15 cc.  $\text{H}_2\text{O}$  were shaken with 3.5 g.  $\text{Me}_2\text{SO}_4$  and 15 cc. 10%  $\text{NaOH}$  for 0.5 hr. Then the treatment was repeated. The mixt. was treated with  $\text{KI}$  and  $\text{KOH}$  then filtered after a few hrs. The iodides were dissolved in hot  $\text{H}_2\text{O}$ , filtered and the cold soln. was treated with  $\text{KI}$  and  $\text{KOH}$ . 0.9 g. palmatine iodide (**J**), m.  $253^\circ$ , were obtained, m.  $238-9^\circ$  from alc. 0.43 g. **J** in 43 cc.  $\text{H}_2\text{O}$ , 4.3 cc. glac.  $\text{HOAc}$ , 4.3 cc. 10%  $\text{H}_2\text{SO}_4$  and 3 g.  $\text{Zn}$  activated with  $\text{PtCl}_4$  were heated 3.5 hrs. on the water bath. The addn. of  $\text{KI}$  pptd. the tetrahydropalmatine hydroiodide, white crystals, and this compd. with  $\text{KOH}$  in alc. gave crystals of the free base (**K**), m.  $148^\circ$  ( $148^\circ$  from alc.).  $\text{CHCl}_3$  was used to ext. the mother liquors. The mixt. of **K** and the synthetic product (Feist) also m.  $148^\circ$ . The  $\text{MeO}$  groups are 4 in no. and not 5. The picrate m.  $165-7^\circ$  in evacuated tubes, the hydrochloride, m.  $249-50^\circ$ , white needles. The methylated **G** was reduced and **K** was also prepd. therefrom. Crystallographic data are given.

H. E. WILLIAMS

**Ring contraction in quinoxaline derivatives and a new method of formation of benzimidazoles.** I. K. BRAND AND E. WILD. *Ber.* 56B, 105-19(1923).—When an alc. soln. of equimol. amts. of  $(\text{PhC}(\text{O})-\text{O})_2$  (**A**), and  $2,4\text{-H}_2\text{N}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{NHC}_6\text{H}_4\text{Me}$  is heated with somewhat more than the equimol. amt. of  $\text{HCl}$ , the expected 1-*p*-tolyl-2,3-diphenyl-6-nitrostilbazonium chloride is not obtained but the  $\text{HCl}$  salt of 1-*p*-tolyl-2-phenyl-5-nitrobenzimidazole (*Bull. soc chim.* [3] 17, 899). A 5-membered ring is obtained in place of a 6-membered one. The condensation of **A**, and  $2,4\text{-H}_2\text{N}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{NHC}_6\text{H}_4\text{NHPh}$  gave benzil-5-nitro-2-phenylaminoanil (**B**) (*Ber.* 31, 2427). The action of concd.  $\text{HCl}$  in alc. transforms this into 1,2-diphenyl-5-nitrobenzimidazole, which was obtained directly from **A** and  $2,4\text{-H}_2\text{N}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{NHC}_6\text{H}_4\text{NHPh}$  by boiling an alc. soln. with  $\text{HCl}$ . 1,2,3-Triphenyl-6-chlorostilbazonium pseudo base,  $\text{C}_{26}\text{H}_{19}\text{O}_2\text{N}_3\text{Cl}$ , prepd. by heating **A** and 4,2- $\text{Cl}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{NHC}_6\text{H}_4\text{NHPh}$  in alc. and pouring into dil.  $\text{HCl}$ , yellow needles, m.  $164^\circ$ . Heating this in alc. with  $\text{HCl}$  does not give the benzimidazole. Likewise, 2,3-diphenyl-6-nitroquinoxaline (*Ann.* 292, 254) was unchanged by this treatment. Benzil-5-nitro-2-methylaminomonoanil (**C**), yellow leaflets, m.  $195^\circ$ . The concd. acid soln. is red. The mother liquors contain 2,3-diphenyl-6-nitroquinoxaline, which was also obtained by heating **C** with alc.  $\text{HCl}$ . If **C** is dissolved in just the requisite amt. of concd.  $\text{HCl}$  with warning, 1-methyl-2,3-diphenyl-6-nitrostilbazonium chloride seps. on cooling as deep

yellow needles, contg. 2HCl and m. 168°. Heating with EtOH regenerated C. If the above HCl soln. is satd. with  $\text{NH}_3$ , the *stilbazonium pseudo base* is obtained as yellow needles, m. 170°; repeated crystn. from EtOH transforms this into C. When 4,2- $\text{O}_2\text{N}(\text{H}_2\text{N})\text{C}_6\text{H}_4\text{NHMe}$  and BzCl are heated in a sealed tube at 220° for 4 hrs., *1-methyl-2-phenyl-5-nitrobenzimidazole hydrochloride* is formed, needles, m. 262°. Recrystn. from EtOH gives the free base, m. 189° (Muttelet, *Bull. soc. chim.* [3] 17, 866 gives 140°).

C. J. WEST

Structure of organic crystals (BRAGG) 2. The structure of benzene (HUGGINS) 2. Polymorphism of antipyrine, vanillin and erythritol (GAUBERT) 2. Dissociation constants of sulfoacetic and  $\alpha$ -sulfopropionic acids (BACKER) 2. Electrolytic preparation of phenylhydrazine (Japan. pat. 40,194) 4.

**Formaldehyde.** G. C. BAILEY and A. E. CRAVER. Can. 228,038, Jan. 16, 1923. MeOH in the vapor phase and an O-contg. gas are brought into contact with an oxide of V as catalyst heated to about 275°.

**Phthalic anhydride.** H. SASA. U. S. 1,443,094, Jan. 23.  $\text{H}_2\text{SO}_4$  is heated to about 150–60° and then permitted to react with nitronaphthalene and Fe at about 300°. Phthalic anhydride is recovered by distn. at 300°.

**Antraquinone and phthalic anhydride.** H. D. GIBBS. U. S. 1,444,068, Feb. 6. The anthracene and phenanthrene of anthracene press-cake are vaporized and oxidized by O with oxide of V, Mo or Cr as a catalyst.

**Butyraldehyde and butyl alcohol.** N. GRÜNSTEIN. Can. 228,438, Jan. 30, 1923. Crotonaldehyde is treated with H in the presence of water to produce PrCHO and Bu alc., the water used being preferably that contained in the product of hydration.

**Condensation products of aliphatic aldehydes.** H. W. MATHESON. Can. 228,441, Jan. 30, 1923. Less than 10% of its wt. of a caustic alkali in aq. soln. is slowly added to an aldehyde at a temp. below 20°. The temp. is maintained for 12–24 hrs. The alkali is then neutralized and the condensation product sepd. by distn.

**Diesters from vinyl esters.** F. W. SKIRROW and J. DICK. Can. 228,127, Jan. 16, 1923. A vinyl ester and the corresponding carboxylic acid are heated in the presence of a catalyst to the temp. of ebullition of the mixt. Ethylidene diacetate is thus prepd. from vinyl acetate and AcOH with an oxide of S as catalyst at 120°.

**Vinyl halides.** H. PLAUSON. Can. 227,883, Jan. 9, 1923. Vinyl halides are produced by treating  $\text{CaC}_2$  with a halogen hydride in the absence of an oxidizing agent. Hg salts may be used as catalysts or increased pressure may be used.

**Cyanamide solution free from dicyanodiamide.** J. H. LIDHOLM. U. S. 1,444,255, Feb. 6.  $\text{CaCN}_2$  is gradually supplied to an aq. soln., which is continuously circulated by a pump, on the suction side of the pump, and  $\text{CO}_2$  is supplied on the pressure side of the pump, to produce a soln. practically free from dicyanodiamide. U. S. 1,444,256 relates to a similar method.

**Trichloro-*tert*-butyl benzoate.** T. B. ALDRICH. U. S. 1,443,552, Jan. 30. Trichloro-*tert*-butyl benzoate, white crystals, m. 34–5°, distg. under reduced pressure without decompn., sol. in org. solvents and nearly insol. in  $\text{H}_2\text{O}$ , not readily saponified but decomposed gradually on boiling with alkali, not decomposed by boiling with concd.  $\text{HNO}_3$ , not volatile in  $\text{H}_2\text{O}$  but slightly volatile with steam, is prepd. by reaction between trichloro-*tert*-butyl alc. and BzCl. The corresponding Br compd. and nitrobenzoic esters may be similarly formed.

**Hexamethylenetetramine.** H. PLAUSON. Can. 227,884, Jan. 9, 1923.  $\text{CH}_4$  is heated, with free O in the presence of  $\text{NH}_3$  to produce  $\text{N}_4(\text{CH}_2)_6$ . A catalyst may be used and the yield may be increased by the use of MeOH vapor.

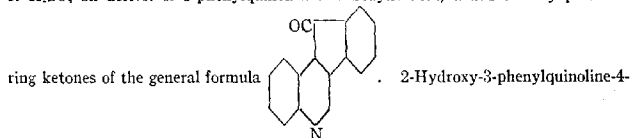
**Oxalate from formate.** H. W. PAULUS. U. S. 1,445,162-3, Feb. 13. Formate is liquefied in a heated receptacle by gradual heating to 220° and then spread upon a hollow heated drum on which it is converted into oxalate by suddenly heating to 360-440°. Cf. C. A. 16, 2868.

**Aromatic arylsulfonyl and similar derivatives of 1,4-naphthylenediamine and its sulfonic acids.** G. T. MORGAN. U. S. 1,442,818, Jan. 23. Toluene-*p*-sulfonyl-1,4-naphthylenediamine, a pinkish white ppt., after crystn., m. 187-8°, is obtained by heating with Zn dust a soln. of 1,4-C<sub>10</sub>H<sub>8</sub>(N:NPh)NHO<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Me in dil. alc. and NH<sub>4</sub>Cl and filtering the resultant soln. into dil. HOAc. Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> also may be used as reducing agent. Benzene-1,3-disulfonylbis-1,4-naphthylenediamine is similarly prep'd. from 1,3-C<sub>6</sub>H<sub>4</sub>(SO<sub>2</sub>NHC<sub>10</sub>H<sub>8</sub>N:NPh)<sub>2</sub>. Other similar compds. may be prep'd. in analogous manner. Directions are given for prep'd. the starting materials which are to be converted into azo compds. for subsequent reduction.

**Hydrocarbons.** HERMAN PLAUSON and G. v. TISCHENKO. Ger. 340,065. Carbides which on treatment with water give C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, or CH<sub>4</sub> are treated, either singly or mixed with steam, at 500-700°. The carbides of Ca, Al, Mn, Ce, La, and U are used. With Ca carbide, a mixt. of hydrocarbons contg. more than 60% of benzene is obtained. A mixt. of Ca and Al carbides at 600° in a vacuum gives pentinene, while at higher pressures polymerized hydrocarbons, *e. g.*, terpenes, are obtained. J. C. S.

**Hydrogenation of unsaturated hydrocarbons.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON. Ger. 350,429. In the hydrogenation of unsat'd. hydrocarbons by passing them, mixed with H, over metallic catalysts a better utilization of the H is obtained by dilg. with CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub>. *E. g.*, in the prep'n. of pure C<sub>2</sub>H<sub>4</sub> from C<sub>2</sub>H<sub>2</sub> the mixt. is diluted with C<sub>2</sub>H<sub>6</sub> until the C<sub>2</sub>H<sub>2</sub> content of the mixt. amounts to less than 30% by vol. Similarly, in the prep'n. of a mixt. of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> the mixt. is diluted with C<sub>2</sub>H<sub>6</sub> or C<sub>3</sub>H<sub>8</sub> until the C<sub>2</sub>H<sub>2</sub> content is less than 35% by vol. J. C. S.

**Ring ketones of the quinoline series.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING. Ger. 343,322. Ring ketones of the quinoline series are prep'd. by the action of H<sub>2</sub>SO<sub>4</sub> on derivs. of 3-phenylquinoline-4-carboxylic acid, which thereby pass into



carboxylic acid when heated with coned. H<sub>2</sub>SO<sub>4</sub> for 2 hrs. at 100° yields a *ring ketone* in the form of orange-red crystals, m. much above 300°; it may be sublimed at higher temps. 2-Hydroxy-3-phenylquinoline-4-carboxylic acid is obtained by condensation, in the presence of alkali, of isatin with phenylacetyl chloride or anhydride, phenylacetyl-ψ-isatin being formed as an intermediate product. It forms light yellow needles which decompose on melting. 2,3-Diphenylquinoline-4-carboxylic acid gives similarly a yellow *ring ketone*. J. C. S.

**Cyanuric triazide.** ERWIN OTT. Ger. 355,926; cf. Ott and Ohse, C. A. 15, 2069. In the prep'n. of cyanuric triazide from cyanuric trihydrazide, C<sub>3</sub>H<sub>4</sub>N<sub>6</sub>, and nitrites (Swiss 89718), the following occur as intermediate products depending on the amt. of nitrite used and the duration of the reaction. Cyanuric dihydrazidomonoazide, C<sub>3</sub>H<sub>2</sub>N<sub>10</sub>, cryst., m. 85-7°; and cyanuric monohydrazidodiazide, C<sub>3</sub>H<sub>2</sub>N<sub>11</sub>, cryst., m. 87-8°. These compds. are less sensitive to percussion than the pure cyanuric triazide, C<sub>3</sub>N<sub>12</sub>. J. C. S.

**Symmetrical aryl alkyl ethers.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. Ger. 343,930. Aryl alkyl halides are heated with alkali hydroxides. Dibenzyl ether is

prepd. by heating benzyl chloride with KOH at 180–200° or with NaOH at 90–120°. It is a colorless liquid with slight blue fluorescence, b. 285–90°. *Ditolyl dimethyl ether* b. 300–10°. The products have uses as solvents. J. C. S.

**Water-soluble derivatives of aryl ethers of higher aliphatic alcohols.** ELEKTROCHEMISCHE WERKE G. M. B. H., HEINRICH BOSSHARD and DAVID STRAUSS. Ger. 344,878. Aryl alkyl ethers, obtained by condensation of naphthols or phenols with halogen-substituted aliphatic hydrocarbons contg. at least 16 C atoms, with appropriate catalysts, are sulfonated until they are sol. in water. *Monochloroparaffin*, obtained by chlorination of paraffin, is a white, wax-like substance, m. 35–40°; it gives, on heating with phenol, K<sub>2</sub>CO<sub>3</sub>, and C in a reflux app., *phenoxyparaffin*, a soap-like mass, m. 60°. The corresponding *sulfonic acid* is a semi-solid, fat-like substance sol. in water. Its dil. aq. soln. may be used for *tanning*. Similar sulfonic acids may be obtained from  $\alpha$ - or  $p$ -tolylloxyparaffin and cetylguaiacol. *Phenoxychloroparaffin*, obtained from *dichloroparaffin* (m. 40–60°) and phenol, and  $\alpha$ - or  $\beta$ -*naphthoxyparaffin* are similar to phenoxy-paraffin. J. C. S.

**Aryl sulfonic esters of halogenated aliphatic alcohols.** GEORG VON KERESZTY and EMIL WOLF. Ger. 353,195. An arylsulfonyl chloride mixed with a halogenated aliphatic alc. is shaken at low temps. with concd. alkali hydroxide soln. until an alk. reaction persists. The ester formed is rapidly hydrolyzed. *Chloroethyl benzenesulfonate*, from benzenesulfonyl chloride and glycol chlorohydrin, b<sub>6–11</sub> 184°. *Bromoethyl benzenesulfonate*, similarly prepd., b<sub>20</sub> 192°. *Dichloropropyl benzenesulfonate*, from  $\alpha,\alpha$ -dichlorohydrin and benzenesulfonyl chloride, b<sub>20</sub> 205° and m. 50°. J. C. S.

***n*-Butyl *p*-aminobenzoate.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE. SWISS 90,590. *p*-Aminobenzoic acid is esterified with *n*-Bu alc., e. g., in the presence of HCl, and heated. On cooling, the *hydrochloride* of the ester crystallizes. By addn. of alkali hydroxide to an aq. soln., the free *n*-butyl *p*-aminobenzoate is pptd. It m. 59°, b<sub>8</sub> 173 4° (cf. Brit. 153,827). J. C. S.

**Thionaphthenesulfonic acid.** GESELLSCHAFT FÜR TEERVERWERTUNG M. B. H. and RUDOLF WEISSGERBER. Ger. 353,932. In the sulfonation of thionaphthene the reaction is conducted in the presence of sufficient Ac<sub>2</sub>O to combine with all the water present in the H<sub>2</sub>SO<sub>4</sub> used, and formed in the reaction. The free acid is a viscid mass, crystallizable with difficulty. The K salt forms colorless platelets. The acid decomposes when heated at 140° with dil. H<sub>2</sub>SO<sub>4</sub>, forming thionaphthene and H<sub>2</sub>SO<sub>4</sub>. J. C. S.

**A derivative of 2-amino-5-hydroxynaphthalene-7-sulfonic acid.** KALLE & Co., AKT.-GES. Ger. 342,733. 2-Amino-5-hydroxynaphthalene-7-sulfonic acid (2 mols.) is heated with *p*-phenylenediamine (1 mol.) in the presence of NaHSO<sub>3</sub>. E. g., by heating at 105° in the presence of NaHSO<sub>3</sub> and NaOH for 12 hrs. and cooling, crystall. condensation products sep. which are freed from NaHSO<sub>3</sub> by heating with HCl. *1,4-Di(5'-hydroxy-7'-sulfo-2'-naphthylamino)benzene* is formed with elimination of NH<sub>3</sub>. This compd. differs from 2,4'-aminophenylamino-5-hydroxynaphthalene-7-sulfonic acid in that it does not form a cryst. Na salt nor give a coloration with a nitrite and alk. resorcinol soln. J. C. S.

**Substituted derivatives of hydrogenated 2-phenylquinoline-4-carboxylic acid, and their salts.** FRITZ ZUCKMAYER. Ger. 344,501. An earlier patent (C. A. 16, 3528) is modified, whereby in place of 2-phenylquinoline-4-carboxylic acid, hydroxy, amino, or acetyl amino derivs. substituted in the quinoline groups, are used. By reduction of 7-acetyl amino-2-phenylquinoline-4-carboxylic acid with Na amalgam, *7-acetyl amino-2-phenyltetrahydroquinoline-4-carboxylic acid* is obtained; it forms yellowish brown crystals, m. 210°, and gives a light yellow *nitroso* compd. The *K salt* is a tasteless, yellow powder. Reduction of 6-hydroxy-2-phenylquinoline-4-carboxylic acid (a yellow mass, m. above



300°) yields 6-hydroxy-2-phenyltetrahydroquinoline-4-carboxylic acid; it is a white, tasteless powder, m. 248-50° (decomp.). The tetrahydro compds. may be acetylated, and form nitroso compds.

J. C. S.

**Tropinecarboxylic acid.** E. MERCK, OTTO WOLFES, and HORST MAEDER. Ger. 354,696. A mixt. of acetonedicarboxylic acid,  $\text{MeNH}_2$  and succinaldehyde is reduced in the cold in neutral, slightly acid, or slightly alk. soln. *E. g.*, a mixt. of Ca acetonedicarboxylate, succinaldehyde, and  $\text{MeNH}_2$  is acidified with AcOH and reduced with 3% Na amalgam, the reaction of the mixt. being maintained acid by addn. of AcOH. After addn. of dil.  $\text{H}_2\text{SO}_4$  and removal of  $\text{CaSO}_4$  by filtration, the filtrate is concd. and treated with KOH. The tropine bases are then extd. with ether. The neutralized alk. soln. is concd. and shaken with MeOH. The MeOH soln., after being freed from salts, contains *tropinecarboxylic acid* in the form of several optically inactive isomerides which are separable with difficulty. One of them is ecgonine from which the *Me ester*, m. 122-6°, can be obtained. The benzoyl deriv.,  $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}$ , m. 79-80°, is identical with optically inactive cocaine.

J. C. S.

**Tropinonedicarboxylic esters.** E. MERCK, OTTO WOLFES, and HORST MAEDER. Ger. 354,950. Succinaldehyde is condensed in alk. soln. with acetonedicarboxylic acid and methylamine and the products of reaction are sepd. without sapon. *E. g.*, solns. of succinaldehyde in water, ethyl acetonedicarboxylate in EtOH, and methylamine and KOH in water are mixed with careful cooling. After several hrs. the reaction products are neutralized with acid. After evapn. of the alc., the residue is treated with  $\text{NH}_3$  and extd. several times with  $\text{CHCl}_3$ . After removal of the  $\text{CHCl}_3$  by distn. from the ext., ethyl tropinonedicarboxylate remains as a viscid, uncrystallizable oil. It differs from the monocarboxylic ester in not forming a solid hydrate with water. Heating the ester with acids yields *tropinone*. The monocarboxylic ester is obtained by careful hydrolysis.

J. C. S.

**Allylarsonic acid.** F. HOFFMANN-LA ROCHE & Co., AKT.-GES. Swiss 89055. Addn. to Brit. 167,157 (C. A. 16, 614). Allylarsonic acid,  $\text{CH}_2=\text{CH}.\text{CH}_2.\text{AsO}(\text{OH})_2$ , forms colorless needles or stout prisms, m. 129-30°. The white Ag salt is sol. in dil.  $\text{HNO}_3$ . The acid decolorizes Br water, and  $\text{KMnO}_4$  soln. made alk. with Na carbonate. The primary Na salt, which forms lustrous leaflets, is not hygroscopic and melts partly at 87-8° in its water of crystn. The aq. soln. is weakly acid to litmus and can be heated to 120° without decompn. The hygroscopic secondary Na salt has an alk. reaction. The acid is decomposed by mineral acids with the sepn. of  $\text{As}_2\text{O}_3$ . The Zn, Pb, Cu, Co, and Fe salts are insol.

J. C. S.

**Ethylene by reduction of acetylene.** JOSEPH-MARIE-ALPHONSE CHEVALIER and PAUL BOURCET. Fr. 526,129. Purified  $\text{C}_2\text{H}_2$  is passed through a soln. of  $\text{CrSO}_4$  (obtained by electrolytic reduction of chrome alum) in the presence or absence of electrolytically prepd. H. The  $\text{C}_2\text{H}_2$  is rapidly absorbed with formation of  $\text{C}_2\text{H}_4$  which can be purified by repeated passage through  $\text{CrSO}_4$  soln.

J. C. S.

**$\alpha$ -Chloronaphthalene derivatives.** KALLE & Co., AKT.-GES. Ger. 343,147. Nitronaphthalene- $\alpha$ -sulfonic acids or naphthosultone- $\alpha$ -sulfonic acids are treated with Cl or chlorinating agents. The sulfonic acid group is thereby replaced by Cl and chloronitronaphthalenes or chloronaphthosultones are formed. 1-Nitronaphthalene-8-sulfonic acid gives, by the action of Cl, HCl, Na and chlorate, or a hypochlorite, 8-chloro-1-nitronaphthalene. Similarly, from 2-nitronaphthalene-4,8-disulfonic acid, 4,8-dichloro-2-nitronaphthalene is obtained; it forms yellow needles, m. 132°. By reduction, 4,8-dichloro-2-aminonaphthalene is obtained, m. 133°. Chlorination of 1-chloro-5-nitronaphthalene-4-sulfonic acid gives 1,4-dichloro-5-nitronaphthalene. 1,5-Dichloro-4-nitronaphthalene is similarly obtained. Na naphthosultone-4-sulfonic acid gives in the same way 4-chloronaphthosultone, m. 181-3°. It yields 4-chloro-1-hydroxynaphthalene-8-

*sulfonic acid* by warming with dil. NaOH soln. This compd. gives by hydrolysis 4-chloro-1-hydroxynaphthalene. The products are used in the prepn. of coloring matters.

J. C. S.


**Preparation of compounds of pyridinebetaine with metallic salts.** LEOPOLD CASSELLA & Co., G. M. B. H. Ger. 343,148. By the action of metallic salts on pyridinebetaine in concd. aq. soln., compds. are obtained which serve as glycerol substitutes. *Dipyridinebetaine sodium chloride*,  $C_5NH_3Cl \cdot CH_2 \cdot CO_2 \cdot C_5NH_3 \cdot CH_2 \cdot CO_2Na$ , is obtained by the action of  $Na_2CO_3$  on dipyridinebetaine hydrochloride; it is a viscid liquid,  $d_{15}$  1.26. *Dipyridinebetaine calcium chloride* has  $d_{15}$  1.28. *Dipyridinebetaine potassium iodide* is a light yellow liquid,  $d_{15}$  1.475. *Dipyridinebetaine mercuric chloride* forms long needles. *Dipyridinebetaine sodium salicylate* is also mentioned. The alkali and alk.-earth metallic compds. are strongly hygroscopic and with the addn. of small quantities of water form viscous liquids having many of the properties of glycerol. They may be crystd. by concn. and cooling.


J. C. S.

**$\alpha$ -Keto-substituted hydrogenated naphthalenes.** GEORG SCHROETER and TETRALIN G. M. B. H. Ger. 352,720.  $\alpha$ -Naphthol and iso- or hetero-nuclear substituted  $\alpha$ -naphthols, melted or in soln., are treated with H under pressure in amt. corresponding with less than two mols., in the presence of metallic catalysts. *E. g.*, colorless  $\alpha$ -naphthol is mixed with tetrahydronaphthalene and a catalyst consisting of reduced Ni deposited on kieselguhr, and treated with H at 120–80° under a pressure of 10–20 atm. After absorption of H corresponding with 1.5 mols., the reaction is ended and the filtered liquid fractionated under reduced pressure. At 14 mm. pressure, the tetrahydronaphthalene distils over at 100°.  $\alpha$ -Ketotetrahydronaphthalene  $b_{14}$  134–5°. The distillate at higher temps. is a mixt. of  $\alpha$ -naphthol and *ar*-tetrahydro- $\alpha$ -naphthol, which is again submitted to reduction.  $\beta$ -Naphthol similarly treated gives no ketone, but a little *ar*-tetrahydro- $\beta$ -naphthol and *ac*-tetrahydro- $\beta$ -naphthol. 1,5-Dihydroxynaphthalene yields similarly, by reduction, 1-*keto*-5-hydroxytetrahydronaphthalene, colorless crystals, m. 156–7°. It forms a semicarbazone, m. 224°, an acetyl deriv., a methyl ether, and a phenylurethan. 1,8-Dihydroxynaphthalene gives, by reduction, 1-*keto*-8-hydroxytetrahydronaphthalene. 1-Hydroxy-5-acetylaminonaphthalene gives 1-*keto*-5-acetylaminotetrahydronaphthalene.

J. C. S.

**Symmetrical octahydroanthracenes.** GEORG SCHROETER and TETRALIN G. M. B. H. Ger. 352,721. Purified anthracene, melted or in soln., is treated with H under pressure in the presence of catalysts. *E. g.*, purified anthracene, m. 214°, is dissolved in tetrahydronaphthalene and in the presence of a catalyst, prepd. by pptn. of reduced Ni on fuller's earth, treated with H at 180–200° under a pressure of 10–15 atm. until a quantity equiv. to 4 mols. is absorbed. The product is fractionated under reduced

pressure. *s*-Octahydroanthracene,  $C_{12}H_{18}$ , , forms crystals, m. 72–3°,  $b_{11}$

160–2°. It forms a monosulfonic acid,  $C_{12}H_{17}$ , . With Cl and Br cryst.

halogen substitution products are formed. By oxidation with  $CrO_3$ , 4-*keto*-*s*-octahydroanthracene is obtained. The symmetrical constitution of the octahydroanthracene is shown by the following synthesis. Tetrahydronaphthalene gives with chloroacetyl chloride in the presence of  $P_2O_5$   $\alpha$ - and  $\beta$ -tetrahydronaphthoylacetyl chlorides,  $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot COCl$ ; the latter give with Et sodiomalonate ethyl  $\alpha$ - and  $\beta$ -tetrahydronaphthoylacetylmalonates,  $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot CH(CO_2Et)_2$ , which by hydrolysis give  $\alpha$ - and  $\beta$ -tetrahydronaphthoylpropionic acids,  $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$ . By reduction, these acids yield  $\alpha$ - and  $\beta$ -tetrahydronaphthylbutyric acids. From the chlorides of these acids cyclic ketones are obtained by inner condensation. From  $\beta$ -tetrahydronaphthylbutyryl chloride,

4-keto-*s*-octahydroanthracene and 4-keto-*s*-octahydrophenanthrene are obtained and may be sepd. by means of their semicarbazones. 4-Keto-*s*-octahydroanthracene yields, on reduction, *s*-octahydroanthracene, m. 72-3°, identical with that prepd. by the catalytic process. Similarly, catalytic *s*-octahydroanthracene gives on oxidation with  $\text{CrO}_3$  4-keto-*s*-octahydroanthracene identical with the compd. obtained in the above synthesis. J. C. S.

**Symmetrical octahydrophenanthrenes.** GEORG SCHROETER and TETRALIN G. M. B. H. Ger. 352,719. Purified phenanthrene, melted or in soln., is hydrogenated in the presence of catalysts. *E. g.*, phenanthrene, purified by treatment with readily fusible or finely divided metals such as Na, K, Cu, Fe, or Ni, or other metallic compds. such as sodamide or Ca carbide, is treated with H at 180-220° at 15 atm. pressure in the presence of a catalyst prepd. by pptg. Ni on fuller's earth. The product,  $b_{18}$  160-70°, is purified by way of its sulfonic acid which by treatment with HCl gives *s*-octahydrophenanthrene. The latter compd. forms crystals,  $m.$  16.7°,  $b_{18}$  167.5°,  $d_{20}$  1.026. Its constitution is demonstrated in the same way as that of the *s*-octahydroanthracene (see above). *s*-Octahydrophenanthrenemonosulfonic acid gives a stable chloride which with dil. aniline soln. yields a cryst. anilide. J. C. S.

**Carbamide from cyanamide.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING. Ger. 301,278. Cyanamide is warmed in acid soln. with the sediment, consisting of ferrosulfuric oxide, obtained from the reduction of nitro compds. by iron. *E. g.*, cyanamide soln. acidified with  $\text{H}_2\text{SO}_4$  is warmed at 80° and a paste contg. 83% of ferrosulfuric oxide is added with shaking. The transformation to carbamide is complete in one hr. In acid soln. no dicyanodiamide is formed; neither in dil. soln., does the cyanamide combine with the  $\text{H}_2\text{SO}_4$ . A smaller amt. of catalyst is needed than where  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}(\text{OH})_3$  is used. J. C. S.

**Hydrogenated anthraquinones.** TETRALIN G. M. B. H. Ger. 346,673. Tetrahydronaphthalene (A) or its derivs. are treated, when gently heated, with anhydrides of aromatic *o*-dicarboxylic acids, especially phthalic anhydride (B) in the presence of  $\text{AlCl}_3$  and with addn. of benzene and similar diluents. The  $\gamma$ -ketocarboxylic acids formed are changed into hydrogenated anthraquinones by condensing reagents, particularly fuming  $\text{H}_2\text{SO}_4$ . A and B give, at 60-70° in the presence of  $\text{C}_6\text{H}_6$  and  $\text{AlCl}_3$ ,  $\beta$ -tetrahydronaphthoyl-*o*-benzoic acid (C), crystals, m. 153-5°, gives with  $\text{Ac}_2\text{O}$  a cryst. acetyl-lactone,  $\text{C}_{24}\text{H}_{18}\text{CO}_2\text{C}(\text{OAc})\text{C}_{10}\text{H}_{11}$ , m. 135°. The methyl ester m. 73-4°. By

reduction of the acid,  $\beta$ -tetrahydronaphthylphthalide and *o*-( $\beta$ -tetrahydronaphthylmethyl)-benzoic acid are obtained. By the action of fuming  $\text{H}_2\text{SO}_4$  on C, a mixt. of  $\alpha$ -tetrahydronaphthanthraquinone [1,2,3,4-tetrahydro-1,2-benzanthrene-7,12-dione], m. 135°, and  $\beta$ -tetrahydronaphthanthraquinone [7,8,9,10-tetrahydronaphthacenequinone], m. 211°, is obtained. The compds. are sepd. by fractional crystn. Both form yellow needles. They yield corresponding anthraquinols on reduction and readily give substituted derivs. with halogens,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ . 2-Methyltetrahydronaphthalene, obtained by the catalytic hydrogenation of 2-methylnaphthalene, colorless oil, b. 219-20°, gives on condensation with phthalic anhydride 3-methyl-2-tetrahydronaphthoyl-*o*-benzoic acid, needles, m. 160°. By the action of fuming  $\text{H}_2\text{SO}_4$  1,2,3,4-tetrahydro-6-methyl-1,2-benzanthrene-7,12-dione is obtained; it forms yellow needles, m. 119°. J. C. S.

**Aromatic selenium compounds.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING. Ger. 348,906 and 350,376. An earlier patent (C. A. 13, 323) is modified by using  $\text{H}_2\text{SO}_4$  instead of Se or  $\text{SeO}_2$  and by substituting other solvents for  $\text{H}_2\text{SO}_4$  or working in the absence of solvents. The compd. obtained from *o*-nitrophenol and  $\text{H}_2\text{SeO}_4$  in the presence of  $\text{H}_2\text{SO}_4$  is a yellow powder contg. 16% of Se, and exploding on heating. Antipyrine gives with  $\text{H}_2\text{SeO}_4$  a compd. contg. 17% Se; it forms small crystals, m. about

238° with discoloration. By the action of selenious oxide on *p*-nitroantipyrine in formic acid soln., *di-p*-nitroantipyrinyl selenide is obtained; it forms yellow crystals, m. about 260° (decompn.). *Di-p*-tolylantipyrinyl selenide,  $(C_6H_4ON_2)_2Se$ , prep'd. from *p*-tolylantipyrine and  $H_2SeO_3$  in alc. soln., forms colorless crystals, m. about 255° (decompn.). The comp'd. obtained by the action of  $H_2SeO_3$  on resorcinol in aq. soln. is a brown powder.

J. C. S.

**N-Nitroso derivatives of secondary amines.** ERICH SCHMIDT and HEINRICH FISCHER. Ger. 343,249; cf. C. A. 15, 87. Tetranitromethane is allowed to react with a boiling alc. soln. of pyridine and a tertiary amine. *o*-Tolylmethylnitrosoamine is prep'd. from *o*-tolyltrimethylamine, diethylnitrosoamine from triethylamine, and diphenylnitrosoamine from diphenylmethylamine. Diphenylnitrosoamine forms light yellow crystals, m. 66.5°. Nitroform, obtained as a by-product, may be reconverted into  $C(NO)_2$ .

J. C. S.

**Naphthosultonesulfonyl chlorides.** KALLE & Co., AKT.-GES. Ger. 343,056. Naphthosultone or its sulfonic acids are treated with chlorosulfonic acid. In the case of naphthosultone, a sulfonyl chloride group enters the 5-position, while in that of the sulfonic acids the sulfo group is chlorinated. The products are very reactive, and may be used in the prepn. of coloring matters. With  $NH_3$  or amines, the sultone ring is broken with formation of sulfonamides or amide-substituted sulfonamide derivs. of the corresponding  $\alpha$ -naphthalenesulfonic acids. By heating Na naphthosultone-3-sulfonate with chlorosulfonic acid at 40–100°, naphthosultone-3-sulfonyl chloride is obtained; it forms crystals, m. 185°. The corresponding anilide m. 212–13°. Naphthosultone-5-sulfonyl chloride, similarly prep'd., forms crystals, m. 194°. The anilide m. 146–7°. Naphthosultone-3,6-disulfonyl chloride forms needles, m. 163°.

J. C. S.

**Acetic anhydride, acetaldehyde, or acetic acid from ethylidene diacetate.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE. Ger. 346,236. Ethylidene diacetate is heated under reduced pressure in the presence of contact substances. The  $Ac_2O$  thus formed is sep'd. by distn. from paracetaldehyde with or without depolymerization or oxidation of the latter. E. g., after heating ethylidene diacetate (400 parts) with  $H_2SO_4$  (8 parts) at 70–80° under 100 mm. pressure, the resultant mixt. of  $Ac_2O$  and paracetaldehyde is either maintained at a medium temp. or heated with a depolymerizing substance, where- by  $ACH$  is obtained and sep'd. by distn. Alternatively, the paracetaldehyde is oxidized to  $AcOH$  by a stream of  $O$ .

J. C. S.

**Quaternary ammonium salts of pyridine-3-carboxylic acid alkyl esters.** RICHARD WOLFFENSTEIN Co. Ger. 343,054. Alkyl pyridine-3-carboxylates are treated with alkyl salts, excepting alkyl halides. Methyl 1-methylpyridine-3-carboxylate methosulfate, obtained by the action of  $Me_2SO_4$  on *Me* pyridine-3-carboxylate, is a light yellow, uncrystallizable oil. The quaternary comp'd. from the action of  $EtNO_3$  on *Et* pyridine-3-carboxylate is a thick, light brown oil. *Am* pyridine-3-carboxylate and  $Me_2SO_4$  give similarly a quaternary comp'd. which is an almost colorless oil.

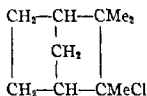
J. C. S.

**O-Alkyl derivatives of hydrocupreine.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. Ger. 344,140. Hydrocupreine oxide, which may be obtained by oxidation of hydrocupreine, is alkylated by the usual methods and the products are reduced to the alkyl derivs. of hydrocupreine. Since the N atom which is alkylated is protected by an O atom,  $NH_4$  bases are not formed. Hydrocupreine oxide (leaflets, m. 199°, obtained by the action of 30%  $H_2O_2$  on hydrocupreine) is treated with  $Et_2SO_4$ ; ethylhydrocupreine oxide sulfate, thereby obtained, forms colorless needles. By heating with excess of  $SO_3$  under pressure, ethylhydrocupreine is obtained. By treatment of hydrocupreine oxide with ethylene chloride and reduction with  $H_2SO_4$  and  $Na_2SO_3$ , chloroethylhydrocupreine is obtained; it forms colorless needles, m. 164°.

J. C. S.

**Camphene hydrochloride.** CHEMISCHE FABRIK AUF AKTIEN FORM. H. SCHERING.

Ger. 348,484. Camphene is treated, in the presence of a suitable diluent, with HCl at low temps. The hydrochloride (formula annexed) thus obtained forms branched



snow-white crystals, m. 125-7°. It has a strong odor similar to

that of menthol, but quite distinct from that of pinene hydrochloride and isobornyl chloride. It is unstable and readily loses HCl, which results in the gradual formation of isobornyl chloride. This transformation takes place more quickly in the presence of acids. By shaking camphene hydrochloride with water, camphene hydrate is formed in quant. yield. The reaction takes place more quickly in the presence of alkalis.

J. C. S.

**1-Amino-2-anthraquinonealdehyde.** LEOPOLD CASSELLA & Co. Ger. 346,188 and Swiss 73,883. The condensation products obtained by heating 1-amino-2-methylanthraquinone with aromatic nitro compds., with or without addn. of primary aromatic amines in the presence of alkalis, are treated with acids. The condensation product

of the compn.  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_2(\text{NH}_2)^1 \cdot (\text{CH}:\text{N-Aryl})^2$  obtained by the action of

1-amino-2-methylanthraquinone on  $\text{C}_6\text{H}_5\text{NO}_2$  in the presence of K carbonate or on  $\beta$ -naphthylamine in the presence of  $\text{C}_6\text{H}_5\text{NO}_2$ , is heated with  $\text{H}_2\text{SO}_4$  or with AcOH and strong HCl. The 1-aminoanthraquinone-2-aldehyde thus obtained forms lustrous, metallic, red crystals, m. 231-3°. The soln. in strong  $\text{H}_2\text{SO}_4$  gives a diazo compd. with  $\text{NaNO}_2$ . When heated with primary amines, it gives an azomethine.

J. C. S.

**1-Alkylpyridinecarboxylates.** E. MERCK. Ger. 344,029. Betaines of the pyridine series are esterified with alics. by the usual methods in the presence of strong acids. The chloride of methyl 1-methylpyridine-3-carboxylate,  $\text{C}_8\text{H}_{10}\text{O}_2\text{NCl} \cdot \text{H}_2\text{O}$ , is prepd. by heating trigonelline or trigonelline chloride with MeOH contg. HCl. It forms colorless crystals, m. 101°.

J. C. S.

**2-ar-Tetrahydronaphthylquinoline-4-carboxylic acids.** CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING. Ger. 344,027. Isatins are condensed with ar-acetyl-tetrahydronaphthalenes in alk. solution. 2-ar-Tetrahydronaphthylquinoline-4-carboxylic acid, from the condensation of isatin with ar-acetyltetrahydronaphthalene, forms dark yellow, transparent leaflets, m. 196-7.5°. With 6-bromoisatin, 7-bromo-2-ar-tetrahydronaphthylquinoline-4-carboxylic acid is obtained; it forms yellow crystals, m. 228-9.5°.

J. C. S.

**Betaines of the pyridine series.** E. MERCK. Ger. 344,030. Pyridinecarboxylic acids are treated with MeCl in alk. soln. at about 100°. Trigonelline is thus prepd. from pyridine-3-carboxylic acid. Pyridine-2,3-dicarboxylic acid (quinolinic acid) gives a methylpyridine-2,3-dicarboxylic acid m. 157°.

J. C. S.

**Hexamethylenetetramine derivatives.** J. D. RIEDEL, AKT.-GES. Ger. 346,383. Ethylene halohydrins are allowed to act, with or without solvents, on hexamethylenetetramine. The additive compd. of hexamethylenetetramine and ethylene chlorohydrin forms crystals, m. 135° (decompn.). The additive compd. of hexamethylenetetramine with ethylene iodohydrin forms rod-like prisms, m. 149° (decompn.).

J. C. S.

**Bromodialkylacetylcarbarnides.** FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. Ger. 347,609; Swiss 92,296. Dialkylmalonic acids of the general formula  $\text{CO}_2\text{H} \cdot \text{CR}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$  ( $\text{R} = \text{alkyl}$ ) are treated with Br with or without addn. of solvents, or diluents, or Br carriers. The reaction proceeds at 100° with elimination of  $\text{CO}_2$ . E. g., diethylmalonic acid is heated with an equal wt. of Br and some  $\text{AlCl}_3$

at 100° under a reflux app. until the evolution of HBr and CO<sub>2</sub> is completed. From the residue, *bromo-α-ethylbutylcarbamide*, m. 118–120°, is obtained with 80–85% of the theoretical yield. J. C. S.

**Monosubstituted sulfonamides.** FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. Ger. 346,810. Sulfonamides are treated with alkylating or arylalkylating reagents in the presence of carbonates. Monosubstituted derivs. of the compn. R.SO<sub>2</sub>NHR' are obtained without the formation of disubstitution products. *p*-Toluene-*p*-sulfonethylamide is obtained by heating toluene-*p*-sulfonamide with NaEtSO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> at 170–200°. *p*-Toluene-*p*-sulfonbenzylamide, m. 115–7°, is similarly prepd. by the action of benzyl chloride on toluene-*p*-sulfonamide in the presence of Na<sub>2</sub>CO<sub>3</sub> or CaCO<sub>3</sub>. J. C. S.

**Crotonaldehyde.** CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE G. M. B. H. Ger. 349,915. AcH vapor is passed over suitable catalysts at temps. below 300°. The crotonaldehyde is removed at once from the seat of the reaction with the excess of unchanged AcH, which is led back again into the reaction chamber, after sepn. from the crotonaldehyde. Charcoal coated with Ti oxide or molds made of Al oxide or hydroxide, Be oxide, Ca(OH)<sub>2</sub>, bog iron ore, cement, or mixts. of these substances are used as catalysts. J. C. S.

## 11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

**Periodicity of the lipase of the stomach.** F. SLUITER. *Nederland Tijdschr. Geneeskunde* 66, I, 2454–5(1922); cf. C. A. 16, 2336.—The activity of the lipase (detd. by mixing equal vols. of milk and of the soln. of the enzyme and titrating the free acid after 24 hrs.) increases and decreases within periods of several days. No explanation for this phenomenon is given. R. BEUTNER

**Chlorophyll and blood pigment.** L. MARCHEWSKI. *Bull. soc. chim. biol.* 4, 476–506(1922).—A review. A. T. CAMERON

**Energy of growth. I. Development of "Aspergillus niger."** E. F. TERROINE AND R. WURMSER. *Bull. soc. chim. biol.* 4, 518–67(1922).—See C. A. 16, 782, 3102, 3931. A. T. CAMERON

**Influence of radioactive substances on acetic fermentation.** E. LABORDE, L. JALOUSTRÉ AND M. LEULIER. *Bull. soc. chim. biol.* 4, 644–7(1922); cf. C. A. 16, 3905.—Development of the activity of *M. aceti* cannot be influenced favorably by addn. of radioactive substances. Addn. of amts. larger than 1 microgram hinders the transformation of EtOH into AcOH. A. T. CAMERON

**Are the active principles of filter-passing and "ultramicroscopic" viruses living organisms or enzymes?** H. M. WOODCOCK. *J. Roy. Army Med. Corps* 39, 243–60(1922).—From a study of the staining reactions it is considered that various filter-passers are not living organisms, but are formed as a result of the breaking down of cell nuclei. A. T. CAMERON

**Imitation of electro-physiological current generation.** R. BEUTNER. *Z. Elektrochem.* 28, 483–9(1922).—A lecture. H. JERMAIN CRIGHTON

**Catalase action of peroxidase.** E. ABEL. *Z. Elektrochem.* 28, 489–96(1922).—A lecture. H. JERMAIN CRIGHTON

**The asymmetric effect of emulsin in the mandelonitrile synthesis.** E. NORDE-

FELDT. *Biochem. Z.* **131**, 390-410(1922).—A study of the conditions for the optimum formation of *d*-PhCH(OH)CN and of some properties of emulsin. The reactions were followed by the polariscope. When emulsin is added to a mixt. of PhCHO and HCN in equimol. concn. there is formed *d*-PhCH(OH)CN. If emulsin is not present *d*-PhCH(OH)CN is produced and the velocity of the reaction is a function of the H-ion concn. In the mixts. contg. emulsin the protcin constituent (globulin) ppts. out and is of itself not catalytically active. If this pptn. is prevented or if the reaction mixt. is made slightly alk. no optically active nitrile is formed. The amt. of nitrile formed is dependent on the amt. of emulsin present and in low concns. of the latter there is a complete proportionality between the rotation reached and the amt. of emulsin. When larger amts. of the enzyme are present the rotation lags behind. The nitrile formed is labile and the rotation decreases without the intervention of enzyme or other catalyzer. The velocity with which the rotation decreases, increases with a temp. coeff. of  $k_t + 10$ :  $k_t$  = about 3.2; decreases with increasing acidity within the range  $p_H = 3$  to 6.5, and reaches the height of the total synthesis velocity first at the neutral point, where both are very large and where the optical activity decreases rapidly. F. S. H.

Smell and specific gravity. J. H. KENNETH. *Nature* **111**, 151(1923).—Oils of cedar, origanum, sandalwood and terebene decrease in the "pitch" or "heaviness and lightness," "dulness and sharpness" in the order of decreasing d. E. H.

The absorption spectra of methemoglobin, and the alleged transformation of methemoglobin into oxyhemoglobin by the action of alkali. G. QUAGLIARIELLO. *Arch. sci. biol.* **3**, 65-86(1922).—Neutral methemoglobin has 4 absorption bands, at  $\lambda$  631  $\mu\mu$ ,  $\lambda$  576  $\mu\mu$ ,  $\lambda$  540  $\mu\mu$ , and  $\lambda$  500  $\mu\mu$ . Alk. methemoglobin has 3 absorption bands; the first at  $\lambda$  600  $\mu\mu$ ; the other 2 are in the same place as the second and third of neutral methemoglobin. The absorption bands in the yellow and green are proper to methemoglobin, and not due to the presence of oxyhemoglobin. A transformation of methemoglobin into oxyhemoglobin through the action of hydroxyl ion is excluded. J. C. S.

Effect of filtration on amylases. JEAN EFFRONT. *Compt. rend. soc. biol.* **86**, 271-3(1922); cf. *C. A.* **16**, 1257.—Ptyalin retained from saliva by filter-paper cannot be removed by water or by sugar soln. It is removable, however, in the presence of NaCl or starch paste. This absorption increases with rise of temp. and affects, not only diastases, but also inhibitory substances accompanying them. Diastases may thus be purified by filtration. Many inactive plant juices may be activated by filtration. J. C. S.

Origin of melanin from pyrrole. II. Action of organ extracts on pyrrole. The sepia of the cuttlefish. PIETRO RONDONI. *Sperimentale* **75**, 33-44(1921); cf. *C. A.* **15**, 868.—An aq. ext. of the ink-sac of cuttlefish (previously freed from secretion) gives a distinct blackening with pyrrole. It is weaker in the case of an ext. heated for ten minutes, but is deepened by addn. of  $FeSO_4$  soln. Similar results are obtained with ext. from frog skin. The phenomenon is confined to malanogenic organs and is of colloidal character. A pyrrole oxidase may be present. The inky secretion (sepia) appears to be a suspensoid associated with a protective colloid which prevents pptn. by the electrolytes in sea water. From the similar properties of sepia and Angeli's "pyrrole-black" it is concluded that a pyrrole ring occurs in the former. J. C. S.

Inhibition phenomena in amylases. II. URBAN OLSSON. *Z. physiol. Chem.* **117**, 91-145(1921).—The optimum reaction for the action of a sample of ptyalin in the presence of NaCl and NaOAc was found to be  $p_H$  6.4. Malt diastase is inactivated more readily than ptyalin. I and F ions have no inactivating influence on malt diastase.  $FeCl_3$  in low concn. activates, in high concns. inactivates malt diastase. On dialyzing ptyalin, an activator is removed which consists chiefly of salts the presence of which is

necessary for the usual diastatic action. The action of various inhibiting reagents is given. It is suggested that the inactivating capacity of some of the heavy metals might be utilized as a means of detecting very small traces of these metals. J. C. S.

**Emulsin.** BURCKHARDT HELFERICH. *Z. physiol. Chem.* 117, 159-71(1921).—A satisfactory method for prepg. emulsin from the kernel of the plum is to mill the stones, ext. the paste with water under toluene for 9 weeks, filter, and ppt. with 95% alc. Prolonged extn. and pptn. from dil. soln. conduce to more potent preps. The enzyme can be purified by dialysis. The conditions for the quant. *estn.* of the activity of  $\beta$ -glucosidases are also described. J. C. S.

**Emulsin.** RICHARD WILLSTÄTTER AND WILHELM CSÁNYI. *Z. physiol. Chem.* 117, 172-200(1921).—The optimum reaction for the hydrolysis of amygdalin by emulsin lies in the neighborhood of neutrality; that of lactose and raffinose more on the acid side. Emulsin preps. kept for about 6 months showed considerable loss of activity. From the difference of the quotients (a) of the hydrolysis of  $\beta$ -methylglucoside, lactose, and raffinose from that of amygdalin, (b) of the hydrolysis of lactose from that of prunasin, (c) of the hydrolysis of  $\beta$ -glucoside from that of prunasin by various preps. from sweet and bitter almonds and apricot kernels, it was concluded that the emulsin reactions were of the nature of independent enzyme reactions, and that the preps. were a mixt. of numerous enzymes capable of degrading glucosides and polyoscs. J. C. S.

**Experiments with invertase.** H. VON EULER AND K. JOSEPHSON. *Arkiv Kemi, Mineral. Geol.* 8, No. 23, 9 pp.(1922); cf. *C. A.* 16, 4215.—Analyses of the Ag-invertase preps. previously described gave ash 1-4, P 1-2%, carbohydrate, hexose, 6-20% (original has 60-20%, ?), pentose less than 5%, total N 5-8%, amino N (Van Slyke) readily reacting (10 min.) 1, slowly reacting (4 hrs.) 2%. P content makes the presence of nucleoprotein improbable. The preps. decolorized Br water, but not I solns. Also in *Ber.* 56B, 446-52(1923). H. B. LEWIS

**Studies in pancreatic function.** Enzyme concentration of duodenal contents after the ingestion of pure foodstuffs and food mixtures by normal men. C. W. McCLEURE AND A. S. WETMORE. *Bost. Med. Surg. J.* 187, 882-95(1922); cf. *C. A.* 16, 276.—The findings showed that the presence of food in the human intestines in some way stimulated the activity of the external secretory function of the pancreas. They indicate that the principal factor in producing this stimulation was the absorption of the products of digestion rather than the acidity of the gastric chyme. Lipolytic activity of duodenal contents was always, while proteolytic and amylolytic activities were almost always, greater after the ingestion of olive oil than after the ingestion of protein or carbohydrate food. From this it is inferred that olive oil was a more powerful stimulant to the activity of the external secretory function of the pancreas than were the other types of food. H<sub>2</sub>O was a less potent stimulant of external pancreatic secretion than were food substances. After the appearance of food substances in the duodenum there was a latent period before the flow of enzymes and bile began. The time coincident of the onset of the flow of bile and pancreatic juice suggests a common stimulant. Under the exptl. conditions employed the fasting duodenal contents contained both enzymes and bile pigments. There is no evidence presented which supports the secretin theory of pancreatic secretion. JULIAN H. LEWIS

Some observations on blood sugar and the alleged glucosuria following operative procedures on the thoracic duct. C. S. WILLIAMSON. *J. Lab. Clin. Med.* 8, 19-22 (1922).—Practically no changes in the blood sugar level were observed following operative procedures on the thoracic duct, (thoracic duct ligation or thoracic duct fistula). Glucosuria did not develop in any of the expts. E. R. LONG

The effect of warm and cold weather on the blood catalase. W. E. BURGE AND J. M. LEICHENRING. *J. Lab. Clin. Med.* 8, 33-6(1922).—As the weather grows colder,



passing from summer to fall and winter, the blood catalase of Illinois rabbits gradually increases, and passing from winter to spring and summer when the weather is growing warmer the blood catalase gradually decreases. The blood catalase of Louisiana rabbits in December is much lower than that of rabbits at the same time in the colder climate of Illinois. However, if the La. rabbits are brought north to Illinois in the winter, the blood catalase rapidly increases. The increase in oxidation in warm-blooded animals brought about by cold weather is attributed to an increase in catalase and the decrease in oxidation brought about by warm weather is attributed to a decrease in catalase.

E. R. LONG

**Hydrolysis of yeast nucleic acid with dilute alkali at room temperature.** (Conclusions of Steudel and Peiser.) P. A. LEVENE. *J. Biol. Chem.* 55, 9-13(1923).—When yeast nucleic acid is treated with 3% NaOH soln. at room temp. as described by Steudel and Peiser (*C. A.* 16, 3490), not only is guanylic acid formed as claimed by them but the other 3 nucleotides appear simultaneously and can be isolated as the brucine salts, thus removing all doubts regarding the tetranucleotide theory of the structure of yeast nucleic acid. The liberation of guanylic acid under these conditions is not complete as claimed by S. and P.; at 25° 12% of the nucleic acid remained unchanged, at 20° 37% and at 15° 52%. "No attempt was made to isolate the individual nucleotides in the free state, since the isolation of the brucine salt is sufficient evidence to prove the contention that the bonds between the individual nucleotides of the yeast nucleic acid are very feeble. Thus the theory of an ester linking between the nucleotides is the one which best harmonizes with the exptl. facts."

A. P. LOTHROP

**The phagocytosis of solid particles. V. Carbon and quartz in solutions of varying acidity.** W. O. FERN. *J. Gen. Physiol.* 5, 311-25(1923).—Leucocytes from the rat ingest quartz particles more readily than C particles in acid solns., but C more readily than quartz in alk. solns. In solns. contg. acacia, C is preferred to quartz even in acid solns. MnO<sub>2</sub> particles are ingested much more rapidly than Mn silicate or quartz. Leucocytes are distinctly attracted towards MnO<sub>2</sub> particles, but not towards C or quartz particles. *Penicillium* spores are ingested more readily than quartz. Very small particles (less than 1 micron in diam.) are less readily ingested than larger particles of the same material. Since this is contrary to the predictions of surface tension, it is suggested that some other factor is involved in this case. Measurements of C electrode potentials and the cataphoretic charges on the particles did not offer an explanation of the relative rates of ingestion of C and quartz at different H-ion concns. C. H. R.

**Conductivity as a measure of vitality and death.** S. C. BROOKS. *J. Gen. Physiol.* 5, 365-81(1923).—The conductance of *Laminaria*, *Saccharomyces*, *Bacillus coli*, *B. butyricus*, *Chlorella* and red blood cells is closely proportionate to and detd. by that of the surrounding fluid with which these tissues are apparently in equil. Changes in conductance of this fluid are quickly followed by compensatory changes in that of the tissue. All tissues, whether alive or dead, offer greater resistance to the current than the surrounding soln. These conclusions are believed to be generally applicable. A quantity, called net resistance, is defined; it is independent of the cond. of the fluid bathing the tissues.

CHAS. H. RICHARDSON

**The ionization of protein chlorides.** D. I. HITCHCOCK. *J. Gen. Physiol.* 5, 383-94(1923).—The concns. of H<sup>+</sup> and Cl<sup>-</sup> were measured in 1% solns. of purified gelatin, egg albumin, casein, edestin and serum globulin contg. 0.001-0.1 N HCl. The results show that these protein chlorides are highly ionized electrolytes, yielding upon ionization a Cl ion and a positive protein-hydrogen ion. Loeb's theory of colloidal behavior is supported (cf. *C. A.* 16, 3098).

CHAS. H. RICHARDSON

**The mechanism of the effect of acids and alkalies on the digestion of proteins by pepsin or trypsin.** A correction. J. H. NORTHPROP. *J. Gen. Physiol.* 5, 415(1923).—

The statement in a previous paper (C. A. 17, 407) that "the amt. of acid required to bring the protein soln. to a given  $p_H$  is independent of the nature and valence of the anion" is literally true only of strong acid. With weak or polybasic acids the amt. required is larger the weaker the acid as shown by Loeb (C. A. 16, 3098). C. H. R.

The influence of electrolytes on the cataphoretic charge of colloidal particles and the stability of their suspensions. II. Experiments with particles of gelatin, casein and denatured egg albumin. JACQUES LOEB. *J. Gen. Physiol.* 5, 395-413(1923); cf. C. A. 16, 4220.—Particles of collodion coated with gelatin and particles of casein and of boiled egg albumin were suspended in  $H_2O$  of different  $p_H$ ; the effect of various electrolytes on the cataphoretic p. d. of these suspensions was measured. The influence of a given electrolyte was about the same for all protein particles. NaCl,  $CaCl_2$  and  $Na_2SO_4$  affected the p. d. of proteins at the isoelec. point but little; salts with a trivalent or quadrivalent ion ( $LaCl_3$ ,  $Na_4Fe(CN)_6$ ) produced a high p. d. on the isoelec. particles,  $LaCl_3$  making them positive,  $Na_4Fe(CN)_6$  negative. This agrees with the action of these groups of salts on the anomalous osmosis through collodion membranes coated with gelatin (C. A. 16, 1786). At  $p_H$  4.0, the proteins have a positive charge, increased by  $LaCl_3$  but not by NaCl or  $CaCl_2$ ; the cataphoretic charge becomes strongly negative under the influence of  $Na_4Fe(CN)_6$ . At  $p_H$  5.8, the cataphoretic charge is negative, strongly increased by  $Na_4Fe(CN)_6$ , affected very little by NaCl or  $Na_2SO_4$ , and becoming strongly positive under the influence of  $LaCl_3$ . "The fact that electrolytes affect the cataphoretic p. d. of protein particles in the same way, no matter whether the protein is denatured egg albumin or a genuine protein like gelatin, furnishes proof that the solns. of genuine proteins such as crystalline egg albumin or gelatin are not diaphasic systems." This work will be extended in a subsequent paper. CHAS. H. RICHARDSON

Biochemical synthesis of an  $\alpha$ -D-mannoside starting from mannans. H. HERISSY. *Compt. rend.* 175, 1110-2(1922); cf. C. A. 16, 1257, 2336.—To 4 l. of 10% MeOH is added 500 g. of ground carob beans, 110 g. of dry powdered lucerne seed and, to exclude microorganisms, 40 cc. of toluene. The mixt. is stirred frequently and allowed to stand at lab. temp. for 80 days. The mixt. is at first nearly solid from the swelling of the albumins, then viscous and finally fluid so as to be readily filtered. The filtrate contains the  $\alpha$ -methyl-D-mannoside, formed by the successive actions of the seminase and D-mannosidase contained in the lucerne powder, the former hydrolyzing the mannans of the bean to a mannose and the latter uniting with the mannose thus produced. Several g. of a cryst. product are obtained which m. at  $193^\circ$ ,  $[\alpha]_D = 79.6^\circ$ . Its aq. soln. does not reduce Cu soln. or form a ppt. with phenylhydrazine acetate. After boiling with dil. mineral acids and neutralizing it gives with phenylhydrazine a ppt. of mannose hydrazone. L. W. RIGGS

Enzymes, oxidants and thermogenesis. G. MARINESCO. *Compt. rend.* 176, 131-3(1923).—By histologic methods it was established that the temp. level of different animals bears a direct relation to the amt. of oxidizing enzymes in the tissues. Bird tissue contained more oxidases than mammalian tissue and much more than the tissue of batrachians. L. W. RIGGS

Mixtures of tartrates and phosphates considered as buffers. Antagonistic action of calcium chloride. L. J. SIMON AND L. ZIVY. *Compt. rend.* 176, 136-8(1923); cf. C. A. 17, 41.—The addition of  $CaCl_2$  to mixts. of tartaric and phosphoric acids causes inverse effects in the neutralization of these two acids. The neutral zone of the one tends to disappear and that of the other to double. Practically the neutral zone and the correlative buffer effect are invariable. The expts. show that the introduction of certain metallic salts may modify the threshold of acidity or of alkalinity and extend the neutral zone of certain buffer mixts. L. W. RIGGS

The influence of the hydrogen-ion concentration on the solubility of uric acid.

A. JUNG. *Helvetica Chim. Acta* **5**, 688-702(1922).—A detailed investigation of the soly. of uric acid at various H-ion concns., produced by the use of the following buffer solns.: 0.1 *N* NaOAc + 0.1 *N* HOAc, [ $p_H$  = 3.24-6.30]; 0.067 *M*  $KH_2PO_4$  + 0.067 *M*  $Na_2HPO_4$ , [ $p_H$  = 5.6-8.2]; 0.1 *M* borax + 0.2 *M* boric acid, [ $p_H$  = 6.77-9.24] [19.1 g. per l.]; 0.1 *M* borax + 0.1 *M* NaOH, [ $p_H$  = 9.44-11.08]. Very steep rises in the soly. curves, most pronounced near the neutral point, occur with increased alkyl. While the various buffers used gave uniform curves, the influence of the anion cannot be regarded as negligible; the steep rises in the alk. region may be due to the formation of complex salts, comparable, perhaps, to the "bound uric acid" of the blood. Similarly the ppt. forming in very alk. solns. probably contains complex salts in addn. to biurate. Shaking with boneblack completely removes uric acid and urates from soln. I. P. ROLF

The sour taste sensation. TH. PAUL. *Umschau* **39**, 610-2(1922).—A resumé of previous work of P. in attempted correlation of acidity with taste reaction. In intermediate concns. (0.005 *N*), the following molar acidities, [*i. e.*, the concn. of substance which in a given vol. gives the same degree of taste reaction as 1 mol. HCl in the same vol. of  $H_2O$ ], referred to HCl as 1, have been assembled:  $H_2CO_3$  0.09, tartar 0.58, HOAc 0.69, lactic acid 0.78, acetyllactic acid 0.85, tartaric acid 1.26. These sp. acidities vary greatly with varying concns., decreasing, especially in the case of substances with high values, with increased concn.; in this as in other respects this sensation shows a close analogy to the sweet taste sensation. I. P. ROLF

Stoichiometric relations between saccharase and silver nitrate. H. V. EULER AND KARL MYRBÄCK. *Svensk Kem. Tids.* **34**, 222-31(1922). (In German. Cf. *C. A.* **17**, 113.)—A definite relation between the inhibition of saccharase and Ag has been established. When the data for 50% inactivation of saccharase by dil. solns. of  $AgNO_3$  ( $2.0 \times 10^{-3}$  to  $3.1 \times 10^{-1}$  *N*) are plotted so that the ordinates represent the  $p_H$  and the abscissas the concn. of  $AgNO_3$  the result is a straight line. The data for the inhibitory effect of 9 concns. of  $AgNO_3$  and variable  $p_H$  from 2.5 to 7 are summarized in a chart. Several preps. were compared and no difference was noted except in one sample considered especially pure. This was more sensitive than the others. The inactivation of Ag is lessened by increase in the enzyme concn. By interpolating the data available in these expts. E. and M. arrived at the following ratios between the saccharase (S) and Ag: mg. S : mg. Ag—0.21:0.0052, 0.25:0.00795, and 0.40:0.008. *i. e.*, Ag equivs. of 4400, 3400 and 5400. A. R. ROSE

Amylases of the cereal grains. RYE. J. L. BAKER AND H. F. E. HULTON. *J. Chem. Soc.* **119**, 805-10(1921).—The enzyme from 100 g. rye acted on 3 l. of 3% starch paste at 50° for 3 hrs. About 22% of the starch was recovered as  $\alpha$ -amylodextrin ( $[\alpha]_D$  184.1°, *R* 1.5) identical with the  $\alpha$ -amylodextrin obtained by the action of the amylase from malted barley (cf. *J. Chem. Soc.* **79**, 1177). The only other product was maltose. An aq. ext. of malted rye acting on 3% starch paste (the enzyme from 1 g. malted rye: 1 g. starch) yielded a non-hygroscopic unfermentable reducing dextrin (*R* 10.8,  $[\alpha]_D$  181.9°) and maltose, but no intermediate maltodextrins such as result when malt amylase is used. GEORGE ERIC SIMPSON

The histidine, arginine and lysine content of lens protein. A. JESS. *Z. physiol. Chem.* **122**, 160-5(1922).—The 3 proteins of the lens,  $\alpha$ -crystallin,  $\beta$ -crystallin and albumoid contain almost the same quantities of these 3 amino acids, *viz.* about 2.63-3.8% of histidine, 7.5-10.26% arginine, and 3.7-4.6% lysine. R. L. STEHLER

Deamination of tyrosine in the animal organism. Y. KOTAKE, Z. MATSUOKA AND M. OKAGAWA. *Z. physiol. Chem.* **122**, 166-75(1922).—On the administration of 10 g. of *L*-tyrosine daily to rabbits hydroxyphenylpyruvic acid was excreted as well as some hydroxyphenyllactic acid. A small amt. of *DL*-hydroxyphenyllactic acid which was isolated is assumed to be of intestinal origin. When *DL*-tyrosine was administered

a portion was excreted as *d*-tyrosine. In one expt. with *dl*-tyrosine a considerable quantity of PhOH, presumably of intestinal origin, was excreted. R. L. STEHLE

**Behavior of phenyllactic acid in the animal organism.** I. Y. KOTAKE AND Y. MORI. *Z. physiol. Chem.* **122**, 176-85(1922).—Dogs, rabbits, and monkeys excrete *d*-phenyllactic acid after the administration of the racemic compd. while men excrete the *l*-form. II. Y. MORI. *Ibid* **122**, 186-90(1922).—*d*- and *l*-Phenyllactic acid (prepd. by fractional pptn. of the strychnine salts) when administered to men and dogs are excreted partially as phenylpyruvic acid. R. L. STEHLE

**Behavior of phenylpyruvic acid in the animal organism.** Y. KOTAKE AND Y. MORI. *Z. physiol. Chem.* **122**, 191-4(1922).—Dogs and men excrete small amts. of *l*-phenyllactic acid after the ingestion of phenylpyruvic acid. R. L. STEHLE

**The behavior of phenylalanine in the animal organism.** Y. KOTAKE, Y. MASAI AND Y. MORI. *Z. physiol. Chem.* **122**, 195-200(1922).—Rabbits excrete phenylpyruvic acid and hydroxyphenylpyruvic acid after the administration of *dl*-phenylalanine by mouth. *d*-Phenylalanine is deaminized by oxidation as well as the *l*-acid. R. L. S.

**The excretion of hydroxyphenyllactic acid after feeding tyrosine to rabbits.** Y. KOTAKE AND M. OKAGAWA. *Z. physiol. Chem.* **122**, 201-5(1922).—About the same amts. of hydroxyphenylpyruvic acid were excreted after the administration of equal amts. of *dl*- and *l*-tyrosine. The latter compd. was not found after feeding *dl*-hydroxyphenyllactic acid. R. L. STEHLE

**The asymmetric reduction of ketone acids to the corresponding hydroxy acids by organs.** Y. MORI AND T. KANAI. *Z. physiol. Chem.* **122**, 206-10(1922).—Hashed organs (liver, kidney and spleen) transform or partly transform phenyl- and hydroxyphenylpyruvic acids into *l*-phenyl- and hydroxyphenyllactic acids. Perfused livers produced the same results. R. L. STEHLE

**The behavior of amino acids in animals colored with vital stains.** I. Y. KOTAKE, Y. MASAI AND Y. MORI. *Z. physiol. Chem.* **122**, 211-19(1922).—Oxidative deamination of phenylalanine and tyrosine was depressed in animals stained with carmine. One rabbit to which *l*-tyrosine had been administered excreted a relatively large amt. of *l*-hydroxyphenyllactic acid. II. *Ibid* 220-4.—The liver of a dog stained with carmine when perfused did not convert phenylalanine into tyrosine as did the liver of an untreated animal. The capacity to form acetone from phenylalanine was not affected. Oxidative deamination is believed to occur in the Kupffer cells which are deeply stained by carmine, while hydrolytic deamination occurs in the parenchyma. R. L. STEHLE

**Acetoacetic acid formation from *d*- and *l*-phenyllactic acids in the surviving liver.** Y. MORI. *Z. physiol. Chem.* **122**, 225-9(1922).—Both members of the first pair form acetoacetic acid; of the second only the *l*-acid does. The members of the second pair were sepd. by fractional pptn. of the morphine salts. R. L. STEHLE

**The formation of urocanic acid from histidine in the dog.** Y. KOTAKE AND M. KONISHI. *Z. physiol. Chem.* **122**, 230-6(1922).—After feeding or subcutaneous injection of histidine urocanic acid (imidazolyacrylic acid) was excreted. Imidazolyllactic acid did not lead to the excretion of urocanic acid. R. L. STEHLE

**Acetoacetic acid formation from urocanic acid in the surviving liver.** M. KONISHI. *Z. physiol. Chem.* **122**, 237-40(1922).—Urocanic acid appears to represent a normal step in the metabolism of histidine inasmuch as the liver converts it into acetoacetic acid. This is also true of histidine and imidazolyllactic acid. R. L. STEHLE

**The deamination of amino acids and the transformations of the resulting products in the animal organism.** Y. KOTAKE. *Z. physiol. Chem.* **122**, 241-4(1922).—A summary of the preceding communications. R. L. STEHLE

**Nucleic acid-protein compounds.** H. STEUDEL AND E. PEISER. *Z. physiol. Chem.*

122, 298-306(1922).—Compds. of clupein with guanylic acid, yeast nucleic acid and eosin were prepd. and shown to consist of equiv. quantities of the protein and acid constituents, *i. e.*, they are apparently definite chem. compds. R. L. STEHLE

The proteolytic enzymes of the kidneys. S. G. HEDIN. *Z. physiol. Chem.* 122, 307-17(1922).—The presence of an erepsin (optimum  $p_H = 7.8$ ) and an enzyme acting upon casein (opt.  $p_H = 4.3-5.6$ ) were demonstrated but no enzymes similar to pepsin or active in alk. soln. could be found. R. L. STEHLE

Jahresbericht über die gesamte Physiologie und experimentelle Pharmakologie mit vollständiger Bibliographie. Edited by P. RONA AND K. SPIRO. Vol. I. Report for 1920. Berlin: Julius Springer. Over 900 pp. \$9.60.

Action of  $H_2O_2$  on  $HCHO$ . Theory of oxidation processes (BACH, GNEROSOV) 10

## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

A physical method for the determination of carbon dioxide in respiratory air. A. K. NOYONS. *Arch. néerland. physiol.* 7, 488-95(1922).—For investigations on metabolism a method is required which makes it possible to read off, at once, several times in a min., the  $CO_2$  content of the respiratory gases. The method devised by N. is based on the fact that the difference of thermal cond. of air ( $N_2$  or  $O_2$ ) and of  $CO_2$  is very considerable—the thermal cond. of  $O_2$  or  $N_2$  being equal to 0.05694, while for  $CO_2$  this value equals 0.0307. The app. is described in detail. It has proved very useful. R. BRUTNER

Microörganisms and low temperatures. D. A. DEJONG. *Arch. néerland. physiol.* 7, 588-91(1922).—The remarkable observation is described that an extremely low temp., *e. g.*, the b. p. of liquid air, is less efficient for annihilating growth of microörganisms than a temp. of  $-20^\circ$ . These results are obtained by exposing various trypanosomes to low temps. Bacteria of the intestinal tract (typhoid bacilli, paratyphoid A and B, colon and others) are found to be resistant at any temp. R. BRUTNER

Ultra-violet luminescence in legal medicine. STOCKIS. *Bull. acad. roy. méd. Belg.* [5] 2, 513-24(1922).—After an extensive review S. describes his own app., which consists of an elec. arc lamp, the electrodes of which are impregnated with Ni salts. The microscopic preps. to be examd. are put on quartz, not on ordinary glass. The prepn. is at first adjusted in ordinary light; after that the luminescence produced by the invisible ultra-violet rays is observed. Solns. of blood remain dark if exposed to the ultra-violet radiation; if, however, the hemoglobin is decompd. into hematin by  $H_2SO_4$ , a distinct luminescence appears. Hematin in urine can also be traced in this way, as well as spots of sperma, pus and various human secretions. Under certain conditions the analysis by luminescence can be used also for the tracing of alkaloids, fats, oils, resins, ink, paper and traces of other substances. R. BRUTNER

A simple method for studying the oxygen-consumption and other vital phenomena of tissues. J. DE HAAN. *Nederland. Tijdschr. Geneeskunde* 65, II, 785-8(1921).—A preliminary description of a method of observing the  $O_2$  consumption of cells. The liquid in which the cells are suspended is made to stream along the cells in order to avoid an accumulation of  $CO_2$ , which influences the respiration. R. BRUTNER

Applications of optical methods to biology. A new apparatus (colorimeter, nephelometer, differential spectroscope). A. BAUDOUIN AND H. BÉNARD. *Bull. soc. chim. biol.* 4, 454-73(1922).—See C. A. 16, 3322. A. T. CAMERON

Estimation of urobilin in blood and cerebrospinal fluid. G. RODILLON. *Bull. soc. chim. biol.* 4, 474-5(1922).—Add to 1 vol. blood serum or cerebrospinal fluid 1 vol. satd.  $Zn(OAc)_2$  soln. in 95% EtOH, stirring with a glass rod. Remove pptd. proteins by filtration or centrifuging. Add to the filtrate alc.-I soln. (2/3%; one drop per 5 cc.),

shake, and add 1/10 the vol.  $\text{CHCl}_3$ . Shake. The  $\text{EtOH-CHCl}_3$  layer contains urobilin combined with Zn. Place against a dark background, and direct the light from a pocket elec. lamp or similar source on the  $\text{CHCl}_3$  layer. If urobilin or its chromogen is present a marked green fluorescence will be visible. If there is a distinct concn. of the pigment the  $\text{CHCl}_3$  will be tinted pink. A small direct-vision spectroscope will show a dark band between E and F, and near F.

A. T. CAMERON

**Micro-method of determination of iron in colloidal solutions.** I. N. KUGELMASS. *Bull. soc. chim. biol.* 4, 577-83 (1922).—For blood, take 0.05 cc., add 2 cc.  $\text{H}_2\text{O}$  in a test-tube, add to the laked blood 0.1 cc. concd.  $\text{HCl}$ , and 1 cc.  $\text{H}_2\text{O}_2$  or other oxidizing agent. Place in a boiling water bath until the soln. and ppt. become white. Cool, add 10 cc. isoamyl alc., then 5 cc. 5 N  $\text{NH}_4\text{CNS}$  (380 g., free from Fe, in 1 l.  $\text{H}_2\text{O}$ ; if necessary free from Fe by adding a trace of alum, then  $\text{NaOH}$ , and filtering rapidly). Mix, and centrifuge. Transfer the amyl alc. layer with a pipet to a colorimeter tube. Prep. a standard soln. by adding 0.5 cc. standard  $\text{Fe}^{+++}$  soln. (0.863 g.  $\text{NH}_4\text{Fe}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$  dissolved in  $\text{H}_2\text{O}$  contg. 5 cc.  $\text{H}_2\text{SO}_4$  and made up to 1 l.; this contains 0.1 mg. Fe per cc.) to 10 cc. isoamyl alc., and 5 cc. 5 N  $\text{NH}_4\text{CNS}$ , mix, and remove the alc. layer for comparison. If a brown ppt. forms on addn. of the thiocyanate, add some drops of 10%  $\text{HCl}$  to both solns. One cc. rabbit blood has an av. content of 0.3 mg.  $\text{Fe}^{+++}$ . For milk ash 5 cc., add to the ash 1 cc. concd.  $\text{HCl}$  and 1 cc.  $\text{H}_2\text{O}_2$ , and proceed as before. One l. cow milk has an av. content of 1.2 mg. Fe. If milk is centrifuged at 10,000 revolutions per min. 3 layers form, an upper (fats), middle, aq., opalescent, and a lower (casein, lecithin, and mineral salts). The first and third contain about the same amts. of Fe; the second contains none. If milk is submitted to ultrafiltration, the filtrate contains no Fe. This suggests that in milk Fe is in org. combination associated in part with proteins, and in part with fats. For waters, evap. 100 cc. to 10 cc. and proceed as usual. For urine, add 2 cc.  $\text{H}_2\text{O}_2$  to 100 cc. of a 24-hr. sample, boil, cool, acidify with  $\text{HCl}$ , add 2 cc.  $\text{CdCl}_2$  soln. and slight excess of  $\text{NH}_4\text{HS}$ . After 1/2 hr. centrifuge, filter, and dissolve by adding to the ppt. on the filter paper warm half-concd.  $\text{HCl}$ . Add to the soln. sufficient 0.1 N  $\text{KMnO}_4$  for complete oxidation, then 10 cc. isoamyl alc. and 5 cc. 5 N  $\text{NH}_4\text{CNS}$ , and proceed as usual. Human urine has an av. content of 0.08 mg. Fe per 100 cc. Ag, Cu, Co, Hg, F,  $\text{PO}_4$ ,  $\text{AsO}_4$ , citrate, tartrate, iodate, and oxalate ions interfere with the reaction. The difference in intensity of the 2 colorimeter tubes should not exceed 25%. The method permits the recognition of 0.01 mg. Fe per l.  $\text{H}_2\text{O}$ ; working with 0.01 mg. Fe the max. error is 2%. The measurement occupies 10 min. A. T. C.

**Some modifications in the measurement of cholesterol by Windaus' method.** R. CAMINADE. *Bull. soc. chim. biol.* 4, 601-13 (1922).—The modified technic for blood is: Ppt. 20-30 cc. serum or plasma with about 70 cc. 95%  $\text{EtOH}$ . Ext. the ppt. in Kumagawa's app. Add the alc. of pptn. and extn. together and conc. *in vacuo* on the water bath to dryness. Ext. 3 times with abs.  $\text{Et}_2\text{O}$ , centrifuge, decant the  $\text{Et}_2\text{O}$  into a beaker, and evap. to dryness by air-current. Treat the residue with 30-40 cc. of a mixt. of acetone 73,  $\text{H}_2\text{O}$  18, and abs.  $\text{EtOH}$  9 parts. Rinse the sides of the beaker. Boil with a very small flame. The residue dissolves (with the exception of lecithin). Remove the flame and add immediately 5 cc. 5% digitonin. Allow to remain some minutes, then filter through a dried weighed filter-paper. Wash this with boiling  $\text{H}_2\text{O}$ , and then with a jet of  $\text{Et}_2\text{O}$  till colorless. Dry 1/2 hr. at 100-110° and weigh. The wt. multiplied by 0.2431 gives the wt. of cholesterol.

A. T. CAMERON

**Technic of the detection of salicylic acid in blood serum and other body fluids.** H. HARRISSEY. *Bull. soc. chim. biol.* 4, 648-51 (1922).—See C. A. 16, 3323. A. T. C.

**A new and efficient respirometer for seeds and other small objects: directions for its use.** G. T. HARRINGTON AND Wm. CROCKER. *J. Agr. Research* 23, 101-16 (1923).—The various methods used to det.  $\text{CO}_2$  are given. A drawing of the new app. is shown.

and the details are described. From the manometer and barometer readings, the temp. observed and the net vols. of the app. used, the 3 significant vols. of air under standard conditions can be calcd. From the 3 vols. it is possible to compute the vol. of  $O_2$  absorbed, that of  $CO_2$  given off and the respiratory quotient. The app. are kept in a bath at const. temp.; the  $CO_2$  is absorbed in NaOH and Hg manometers are used. The methods of recording data and of calcg. results are shown. F. C. COOK

**A metabolism crate for calves and other small ruminants.** A. C. McCANDLISH AND FORDYCE ELY. *J. Dairy Sci.* 5, 565-9(1922). E. J. C.

**Determination of arsenic in the urine.** F. Urtz. *Südd. Apoth.-Ztg.* 62, 453(1922).—U. discusses the excretion of arsenic in the urine and reviews the methods for its estn.

A. G. DuMaz

**A micro-method for the quantitative determination of acetone and  $\beta$ -hydroxybutyric acid in urine and blood.** A. LUBLIN. *Biochem. Z.* 133, 626-41(1922).—For the detn. in urine see *C. A.* 17, 117; in blood see *C. A.* 17, 781. F. S. HAMMETT

**Color analysis of urine. IV. The diazo reaction of urine and urochromogen excretion.** M. WEISS. *Biochem. Z.* 134, 269-91(1922).—Twenty-four cc. of sulfanilic acid soln. are measured into a graduate, 1 cc. 0.5%  $NaNO_2$  is added and the mixt. shaken several times. The standard soln. contains 1:1250 or in 3 cc. 0.0024 g. pure diazobenzene-sulfonic acid instead of 0.002 g. in 5 cc. as directed by Ehrlich. In a deep container exactly 5 cc. of the standard soln., 3 cc. of the diazo reagent and 1 cc. of 20% NaOH are mixed. Measurements are to be made by pipet. The standard color thus produced is a beautiful red and is stable for at least a week. The standard soln. is stable for months. Urine is dild. as necessary; after neutralization to a weakly acid reaction, it is similarly diazotized and compared with the standard. Various compds. found in urine were tested for their reaction with this reagent. Pure solns. of glucose in 0.2% give the reaction after 2 mins. but weakly, later more strongly. Nevertheless, the addn. of glucose up to 10% to urine never resulted in a positive test nor did diabetic urine free from acetoacetic acid. Hence glucose in urine does not participate in the test. Urines which contain acetoacetic acid give a positive test. Although urobilinogen and bilirubin give an egg-yellow color, they can be salted out with  $(NH_4)_2SO_4$  as well as protein without loss of urochromogen. The excess  $(NH_4)_2SO_4$  can be removed by pptn. with 95% alc. Various phenol substances, tyrosine, hydroxy acids, imidazole derivs., albumin, peptone, pyrrole, indole, tryptophan, sarcoma and phenol melanogens, and various drugs known to be excreted in the urine were tested and various results recorded. Notwithstanding the fact that the diazo reaction is so generally given W. believes that it can be used under carefully controlled conditions for the detn. of urochromogen. F. S. HAMMETT

**A clinical method for the approximately quantitative determination of the excretion of urobilin.** A. ADLER. *Deut. Arch. klin. Med.* 138, 309-20(1922).—The method is a modification of that of Schlesinger (*Deut. med. Wochschr.* 1903). It is applied to the detn. of urobilin in the urine, stools and duodenal contents. JULIAN H. LEWIS

**The action of proteins and blood serum on colloidal gold solution and its quantitative interpretation.** PAUL REZNIKOFF. *J. Lab. Clin. Med.* 8, 92-103(1922).—Solns. of pure serum albumin, serum euglobulin and serum pseudoglobulin were tested against colloidal Au soln. and found to have definite and characteristic curves for each protein. These curves depend upon the concn. of the protein in soln. that acts as a protecting or pptg. agent of the colloidal Au. Curves for mixts. of the 3 proteins showed the influence of the individual proteins to correspond to their concn. in the mixts. The filtrate from blood serum deproteinized with 95% alc. has little or no effect on colloidal Au. The colloidal Au reaction is a protein phenomenon. Human sera show marked differences in their effect on colloidal Au soln. in various clinical conditions. In various clinical conditions the amt. of protein N and the % of albumin and globulin

found in sera vary greatly. The curves are influenced by the variations in albumin-globulin ratio. Howe's method for isolating the globulin was not found to be accurate. Serum albumin has a distinct pptg. effect on colloidal Au in certain definite concn. (contrary to Fischer).

E. R. LONG

**The estimation of uric acid in blood.** H. BROWN AND G. W. RAIZISS. *J. Lab. Clin. Med.* 8, 129-34(1922).—Adsorption of uric acid does not take place in the pptn. of blood proteins by the method of Folin and Wu. Equally good recoveries of added uric acid can be obtained either by the method of Folin and Wu or Benedict. Folin and Wu's method gives correct results for blood uric acid, while the high results found with Benedict's method are due to interfering substances. Benedict's reagent is selective and yields results approx. similar to those of Folin and Wu only with high uric acid content. Benedict's method, owing to its speed and requirement of small quantities of blood, can be used for routine clinical analyses, but is not to be recommended for research purposes.

E. R. LONG

**A new method for sterilizing proteins and other colloidal compounds without denaturation.** C. A. MILLS. *J. Lab. Clin. Med.* 8, 134-6(1922).—Protein solns. can be completely sterilized without alterations in their properties by letting stand the required length of time with the proper concn. of  $\text{HgCl}_2$ , the ppt. being redissolved and the Hg rendered dialyzable by addn. of NaCl. The Hg and salt may then be removed by dialysis, Cu being placed outside the dialyzing tube to amalgamate with the Hg.

E. R. L.

**Lead studies. II. A critical note on the electrolytic determination of lead in biological material.** A. S. MINOT. *J. Biol. Chem.* 55, 1-8(1923).—"Denis and Minot (*C. A.* 13, 2380) have described a procedure for the electrolytic detn. of Pb in which Mn is often present in the elec. bath and is deposited with the Pb as  $\text{MnO}_2$  on the anode. This method often gives a positive test for Pb when no Pb is present because  $\text{MnO}_2$  is deposited, which gives the reactions of  $\text{PbO}_2$  in the subsequent steps in the procedure. In the Denis and Minot procedure there are losses of Pb (a) during washing due to soln. of the pptd. sulfides, and (b) due to incomplete elec. sepn. The errors due to deposition of Mn and loss of Pb tend to balance each other and give roughly quant. results. Fairhall's chromate method (*C. A.* 16, 2160) is more accurate and practical than an electrolytic method, though with some modification the Denis and Minot method could be made satisfactory."

A. P. LOTHROP

**The absorption of pepsin by filter paper.** JEAN EFFRONT. *Compt. rend. soc. biol.* 87, 1058-9(1922).—Pepsin solus. of different concn. are mixed with 10 g. filter paper pulp, left to stand 12 hrs., then filtered with suction and the pepsin content is detd. by Fuld's method. The results showed that there is much variation in the absorbing power of different grades of filter paper, certain grades being entirely ineffective while others caused complete adsorption of the enzyme. This difference is attributed to the phys. characteristics of these papers. The adsorption also depends upon the concn. of pepsin, being greatest with a 0.1% soln., and disappearing entirely with 0.5% soln. The reaction of the medium is apparently without any influence and there is also no difference in the rate of absorption between 20° and 40°.

S. MORCULIS

**The nitrogen content of pepsin.** JEAN EFFRONT. *Compt. rend. soc. biol.* 87, 1059-61(1922).—Purification of pepsin: 1 g. of pepsin is dissolved in 1 l. of physiol. salt soln. and mixed with 50 g. of pulp prepd. from filter paper "Dreverhoffs No. 402." This is left at 20° for 17 hrs., and filtered with suction. The residue is again extd. with water and filtered. The N content and the pepsin activity of both filtrates and of the paper pulp were detd. The pulp retained as much as 83% of the activity but retained only 7 mg. of N from a total of 133 mg., 126 mg. being found in the filtrate. A much purer enzyme was prepd. by this method containing only 0.4 mg. (?) N but with



very great proteolytic action. The pepsin can be almost completely deprived of its N and wt. for wt. a prepn. is made which has 5 times the peptic action of the original pepsin.

S. MORGULIS

**A method for the quantitative determination of trypsin and pepsin.** J. H. NORTHROP AND R. G. HUSSEY. *J. Gen. Physiol.* 5, 353-8(1923).—For trypsin digestion, isoelec. gelatin was dild. with 0.1 M  $\text{Na}_2\text{HPO}_4$  to a concn. of 3 g. gelatin (dry wt.) per 100 cc., then brought to  $p_H$  7.4 with 0.1 M  $\text{H}_3\text{PO}_4$ . For pepsin digestion, the same gelatin concn. was brought to  $p_H$  3 with dil.  $\text{H}_3\text{PO}_4$ . The enzyme solns. were prepd. as previously described (*C. A.* 16, 1597-8). 50 cc. of gelatin soln. and 0.5 cc. of various trypsin or pepsin dilns. were mixed at 34°. 10 cc. of the mixt. were placed in each of several viscosimeters (Ostwald type) held in a water bath at 34° and the rates of outflow detd. The actual times in secs. required for the digestion mixt. to pass between the 2 chosen points on the viscosimeter were plotted as ordinates against the time intervals of observation as abscissas. From curves so obtained, it is found that the time required to cause a given % change in viscosity is almost inversely proportional to the amt. of enzyme present. Enzyme reactions which take place in the presence of buffer salts may be studied by this method.

CHAS. H. RICHARDSON

**Determination of total non-protein nitrogen of serum.** Choice of a suitable desalbuminant. P. CRISTOL AND M. SIMONNET. *J. pharm. chim.* 26, 293-309(1922).—See *C. A.* 16, 4221.

S. WALDBOTT

**Laboratory apparatus for the rapid drying of organic substances without decomposing them.** J. BOUILLOT. *J. pharm. chim.* 27, 23-8(1923).—The app. is essentially a strong test-tube of one piece with 2 lateral similar tubes. The boat contg. the material to be dried is put into the horizontally placed test-tube which is closed with a rubber stopper. Into each of the 2 upright tubes a glass tube with curved capillary end is tightly inserted. One glass tube connects with the suction pump, the other with a  $\text{H}_2\text{SO}_4$  drier for the air or inert gas to be used. Stopcocks suitably placed permit the maintenance of a vacuum, and the whole app. may be set into a space of desired uniform temp. The app. is very efficient.

S. WALDBOTT

**The microchemical demonstration of reducing carbohydrates.** STÜLER. *Centr. allgem. Path.* 33, 89-96(1922).—A method for demonstrating sugar in animal tissue is described, based on the methods used in plant histology, which depend on reduction of a satd. alc. soln. of Cu acetate and NaOH. For details the original article must be consulted.

H. G. WELLS

## C—BACTERIOLOGY

A. K. EALLS

**The disinfecting action of ether vapors on pus bacteria.** E. PHILIP. *Munch. med. Wochschr.* 69, 1112-3(1922).—Various kinds of bacteria differed much in their resistance to ether vapors, and the same is true for various strains of the same kind. S. A.

**Digestibility of bacteria.** C. E. DUKES. *Brit. Med. J.* 1922, I, 430-2.—Bacteria do not adsorb proteolytic enzymes. The protein of bacteria is protected from enzymic action by a lipoidal envelope. Antibodies present in immune serum do not render bacteria more digestible by trypsin.

A. T. CAMERON

**Lipin-protein in relation to the acid-fastness of bacteria.** E. R. LONG. *Am. Rev. Tuberculosis* 6, 642-8(1923).—Bacilli of the acid-fast group, which have been defatted as thoroughly as possible with alc. and petr. ether, and from which 20-35% of the dry wt. has been removed in material sol. in petr. ether, remain morphologically intact and acid-fast. Such bacilli still contain from 1 to 8% of the dry wt. in the form of lipin firmly bound to protein in a union, chem. or phys., of such sort that extrn. with fat solvents is impossible. The great variance in the amt. present, calcd. in % of the total dry wt.,

suggests that the union is not a chem. one. This lipin may be rendered extractable in petr. ether by treatment, during 48 hr., of the once defatted bacilli with  $NHCl$ . Simultaneously the integrity of the bacterial cell and its acid-fastness disappear. The lipin removable after the acid treatment appears to be the same in all the microorganisms examd. It has the same characteristic as the wax more easily isolated from the tubercle bacillus and is probably a mixt. contg. the mykol of Tamura and mykol laurate. *B. subtilis*, which is non-acid-fast and which has a low total lipin content, contains the same firmly bound lipin in the same amt. as is found on the av. in acid-fast bacilli, about 5% of the dry wt. However, while this firmly bound lipin usually makes up considerably less than 30% of the total lipin in acid-fast bacilli, it makes up over 50% in the case of *B. subtilis*. It is thought that the disposition of the lipin-protein plays a role in acid-fastness. The finding of similar lipin-protein in *B. subtilis*, which is non-acid-fast, requires the conception of a different manner of disposition in the 2 types of microorganisms.

H. J. CORPER

**The lipin content of acid-fast bacilli.** E. R. LONG AND L. K. CAMPBELL. *Am. Rev. Tuberculosis* 6, 636-41(1922).—Tubercle bacilli of human, bovine and avian types, leprosy, frog, turtle, smegma, dung and grass bacilli, *B. subtilis*, and a strain of *Staphylococcus aureus* were examd. for lipin content. The bacilli of the acid fast group were found rich in lipin as compared with non-acid-fast bacilli. In most cases 20 to 35% of the dry wt. can be extd. with petr. ether after dehydration with hot alc. Qualitatively, there is a great difference in the lipin exts. The bacilli fall into 3 groups as respects the proportion of the total lipin which is present as wax (non-saponifiable lipin). This wax consists of a difficultly hydrolyzable combination of fatty acid with an alc. of high mol. wt. The lipin of the human and bovine type tubercle bacilli is 60 to 77% wax. That of avian type tubercle bacilli, the so-called leprosy bacilli, and the so-called tubercle bacilli of frogs and turtles, ranges between 27% and 36% wax (the higher value being for avian bacilli). The wax content of smegma, dung and grass bacilli of various types ranges from 4 to 10% of the total lipin. A closely similar grouping of the same series has been made on the basis of nutrition. A similar grouping as respects virulence is obvious although not stressed without further study. Sufficient data have been secured to show that the microorganisms listed build wax somewhat in proportion to their glycerophilism and therefore glycerol may be looked upon as a wax progenitor.

H. J. CORPER

**Some microbiologic consequences of the oxidizing properties of thorium X.** P. LEMAY AND L. JALOUSTRE. *Compt. rend.* 175, 1053-4(1922).—The growth of the anaerobic *Bacillus butyricus* in a suitable culture contg. 200 micrograms of Th X was hindered, while the growth of the aerobic *Bacillus lacticus* under similar conditions was facilitated. The cultures were kept under vaseline oil, thus excluding atm. air, and therefore the observed differences from the controls due to oxidation were very marked. The authors conclude the expts. indicate that the oxidizing properties of Th X exhibited in chem. expts. (*C. A.* 16, 1701) are also exhibited in microbiologic phenomena.

G. FAILLA

**Gas production by an aerobic spore-bearing bacillus.** HENRIETTA LISK. *J. Am. Water Works Assoc.* 10, 139-44(1923).—Results from several sources seem to agree as to the characteristics of *B. asterosporus*.

D. K. FRENCH

**The preparation of nucleic acid from the nucleoprotein of tubercle bacilli (tuberculinic acid).** T. B. JOHNSON AND E. B. BROWN. *J. Biol. Chem.* 54, 721-30(1922); cf. *C. A.* 16, 3905.—One lot of dried human tubercle bacilli and one of mixed human and bovine bacilli were extd. 5 or 6 times with toluene at 90-100° for 7-8 hrs. at a time. This removed 34.6 and 43.5%, resp., of the total wt. The dried ext. contained 2.23% ash, of which 54.6% was  $P_2O_5$ , 24.3% was  $CaO$  and 8.7%  $MgO$ . The residue from the

toluene ext. lost 8.2% when extd. with hot 95% EtOH, apparently largely phosphatides. The dried residue from the toluene extn. was ground in 100 g. lots, with 2000 cc. 3% NaOH for 1 hr. and was then acidified with HOAc, the temp. being kept below 20°. After standing overnight, the mixt. was filtered and washed with 2% HOAc. The residue was ground with 1000 cc. 5% NaOH for 2 hrs., was then acidified with HOAc, allowed to stand and filtered. The HOAc filtrates were separately treated with concd. HCl until a slight permanent ppt. was produced, when an equal vol. of 95% EtOH was added, the mixt. being kept cool throughout. After several hrs. the clear supernatant liquid was decanted and the ppt. more completely sepd. by centrifuging. It was washed in succession, with 50%, 95% and abs. EtOH on the centrifuge and then with Et<sub>2</sub>O and was finally dried over concd. H<sub>2</sub>SO<sub>4</sub>. The 2nd ext. yielded only small amts. of acid. The total yield was 7.7 g. acid from 436 g. of the toluene-extd. bacilli. The prepn. did not give the biuret reaction. The dried residue from the NaOH-HOAc extn. of 100 g. of defatted bacilli weighed 84 g. and contained 1.19% P<sub>2</sub>O<sub>5</sub>, or 54.3% of the amt. present before the NaOH-HOAc extn. Since no tests for pyrimidines were obtained, it was concluded that this P was not present as nucleic acid. Analysis by Van Slyke's method gave the following results: amide N 11.83%, humin N 4.11%, cystine N 1.26%, arginine N 10.63%, histidine N 11.48%, lysine N 3.69%, monoamino N 47.39%, non-amino N 9.34%, tryptophan present.

I. GREENWALD

**The proteolytic enzymes of the diphtheria bacillus and their significance for growth and toxin formation.** K. G. DERNEY AND S. SIWA. *Biochem. Z.* 134, 1-19(1922).—When diphtheria bacilli are cultured in bouillon, proteins and peptone are split. This splitting does not begin immediately with growth, but lags behind some 4 to 6 days when the bacilli apparently are autolytically disintegrated. There is little or no proteolytic enzyme in filtered bouillon in which diphtheria bacilli have been grown. Hence this organism does not produce an extracellular active enzyme such as does *B. subtilis*, etc. A weakly active proteolytic enzyme can be detected in macerated autolyzed diphtheria bacilli. This enzyme liquefies gelatin and splits peptone. Since the optimum for the latter activity lies between  $p_H$  6.0 and 7.0 it is probably due to a trypsin-like substance. The absence of a strong extracellular proteolytic enzyme signifies that the nutrient medium for the growth of the organism should contain adequate protein-split products. It is possible that the destruction of the toxin on long-continued culturing is not primarily due to increased alk. but to the autolytic enzymes of the disintegrated microorganisms.

F. S. HAMMETT

**Bacteria which split nucleoproteins and their significance in the liberation of phosphorus in soils.** A. KOCH AND A. OELSNER. *Biochem. Z.* 134, 76-96(1922).—The  $(NH_4)_2MoO_4$  method for the detn. of P can be used for the differentiation of org. P in nucleic acids and the inorg. P derived therefrom by decompn. Ultrafiltration through the Zsigmondy membrane filter provides a sufficiently exact sepn. of bacteria growth of the order of magnitude of the coli bacteria from the culture medium and even holds back the viscous org. constituents of the nutrient soln. which disturb the pptn. in the filtrate. The org. P of the nucleoproteins of nuclear material is quickly split off in inorg. form in the soil by a group of microorganisms called *Nucleobacter*. This liberated P (phosphate) is partly used as foodstuff for the higher plants immediately, and partly laid down in the bacterial cells themselves and reliberated on their death. Ca also plays a part in the reaction, since under its influence nucleic acid and inorg. P are liberated from nuclein. Moreover, the presence of Ca favors the activity of the *Nucleobacter* since it produces an alk. reaction in the soil. The plant residues from the harvest of the previous season which contain P are eventually made available as foodstuff for the new crop by virtue of the soil bacteria.

F. S. HAMMETT

**The metabolism of pathogenic bacteria.** H. BRANN AND C. E. CAHN-BRONNER.

*Klin. Wochschr.* 1, 1824-6(1922).—In studying the metabolic activities of microorganisms on simple foodstuffs, it is essential that the medium be a liquid one composed of the very purest chemicals and redistd. water. Solid media contg. agar cannot be used because of the uncertain compn. of the agar. To be certain that a microorganism can obtain its nutritional requirements from a certain set of simple chemicals, it is essential that the organism be reinoculated into that medium a large number of times, for small traces of the complex nutrient medium upon which the stock culture was grown may facilitate growth and lead to erroneous conclusions. On simple synthetic media, the concn. of available free O is an unusually important factor; many otherwise facultative organisms will not grow upon a simple medium when the O supply is restricted. The investigations were carried out with strains of typhoid, paratyphoid A and B, Shiga-Kruse and colon bacilli. The nutrient medium contained NaCl, phosphate,  $\text{NH}_3$  as the only source of N except in special cases where glycine, alanine, asparaginic acid, leucine, tyrosine, urea, uric acid, or hippuric acid were used, with either formic, oxalic, lactic, succinic, malic, tartaric, or citric acids, glucose or arabinose as sources of C. Organisms of the colon typhoid group that are ordinarily facultative usually grow very well on a medium contg.  $\text{NH}_3$  as the only source of N, and lactic or citric acids as the only source of C. When, however, the O supply is restricted, these organisms do not grow at all. The addn. of glucose alone or in conjunction with the amino acids named above does not induce the organism to grow anaerobically. For the anaerobic development of this group, glucose and tryptophan are essential constituents of the medium. The Shiga-Kruse bacillus develops its typical toxin on a medium contg.  $\text{NH}_3$  and lactic acid. Such simple media can also be used for the development of typical enzymes. The closely related org. acids employed are not equally efficient as sources of C. Examples of such differences are given. Different strains of organisms belonging to the same group may also show marked differences in their nutritional requirements. This is particularly true of the N source. Thus, out of 64 strains of typhoid bacilli, 12 were able to grow on a medium contg. only  $\text{NH}_3$  as a source of N; the other 52 would not grow unless tryptophan was present. These organisms were identical in every other way. Strains of grossly non- $\text{NH}_3$ -using typhoid bacilli may contain a small no. of  $\text{NH}_3$  users. By inoculating large quantities of such strains into a simple  $\text{NH}_3$ -containing medium, the  $\text{NH}_3$  users begin to grow and can be cultivated. MILTON HANKE

**Action of acid, potassium iodide, hydrogen peroxide mixtures on bacteria.** E. JACOBITZ. *Klin. Wochschr.* 1, 2328-30(1922).—*Methods.*—The microorganisms (streptococci, staphylococci, diphtheria bacilli and anthrax spores) were either suspended in the liquids to be tested (suspension method) or, a bit of muslin cloth (1 sq. cm.) was immersed in the bacterial suspension for  $\frac{1}{2}$  hr., the cloth removed and transferred to the liquid (M. C. method). *Results.*—Contact with a 5%  $\text{H}_2\text{BO}_3$  soln. for 24 hrs. does not kill staphylococci. The organisms survive a 6-hr. immersion in 5% HOAc, but are killed in 1 hr. by contact with 5% solns. of tartaric and citric acids. KI in 2 or 5% solns. destroys staphylococci in 15 min. A 3%  $\text{H}_2\text{O}_2$  soln. is completely bactericidal in 1 hr. Liquids were prepd. contg. KI 2 g., acetic, tartaric, citric or boric acid 2 or 5 g., and water to 100 cc. One cc. of each of these liquids was then mixed with 1 cc. of a 3%  $\text{H}_2\text{O}_2$  soln. and 1 cc. of bacterial suspension or 1 sq. cm. of bacteria-satd. muslin cloth. All of these liquids, excepting the boric acid solns., killed the bacteria in 5 min. by the M. C. method, and in 1 min. by the suspension method. The  $\text{H}_2\text{BO}_3$  solns. were completely bactericidal only after 0.5 hr. Very resistant anthrax spores were unaffected by a 7 day contact with the  $\text{H}_2\text{BO}_3$  and HOAc mixts., but had been rendered incapable of development after a 4 hr. immersion in the citric and tartaric acid mixts. **The treatment of wounds with acid, potassium iodide, hydrogen peroxide mixtures.** URBEL. *Ibid* 2330-32.—A soln. contg.  $\text{H}_2\text{O}_2$ , KI and HOAc is reported to give excellent

results in the treatment of wounds, abscesses, etc. The principles of the above abstract are embodied.

MILTON HANKE

A new medium for the isolation of *B. diphtheriae*. S. R. DOUGLAS. *Brit. J. Exptl. Pathol.* 3, 263-7(1922).—The medium consists of agar and serum, of which the antitryptic action is neutralized, together with K tellurite as an indicator. H. F. H.

The metabolism of bacteria. The significance of free amino acids, demonstrated by the indole reaction. ERICH ZDANSKY. *Centr. Bakt. Parasitenk., I. Abt.* 89, 1-3 (1922).—The indole reaction is produced sooner and more intensively in media made with Roche peptone than in media with Witte peptone. This is because the former contains more tryptophan, not only as a free amino acid but combined in the form of polypeptides. This difference produces not only a ready source of indole but better conditions for initial growth.

JULIAN H. LEWIS

The use of mushroom extract as a substitute for meat extract in making culture media. E. WIEGERT. *Centr. Bakt. Parasitenk., I. Abt.* 89, 109-10(1922).—Instead of using meat or meat ext. 50 g. of dried mushrooms are boiled in 500 cc. of  $H_2O$  to which 2 g. of NaCl are added.

JULIAN H. LEWIS

The occurrence of volutin in fungi. ZIKES. *Centr. Bakt. Parasitenk., II Abt.* 57, 21-45(1922).—Volutin is the name that has been given to the metachromatic granules occurring in fungi. Most fungi produce only moderate amts. of volutin. It is produced most in the *Mycoderma* and beer yeasts, less in certain urine yeasts and less in the *Apiculatus* yeasts. These granules react differently with vital staining in the various fungi, many staining red and others blue. Their formation is stimulated in peptone media, less in asparagine and  $(NH_4)_2SO_4$  media. For the formation of volutin P must be present. Volutin-free fungi again produce these granules if P is added to the cultures. More volutin is formed in concd. malt wort than in dil. Glucose and fructose stimulate its formation more than the higher sugars. The fermentation ability of the yeasts is not related to the formation of volutin. In young cells the volutin occurs in the form of very fine tender droplets which combine later to form larger drops. In old cells they gradually disappear. The optimum temp. for volutin formation is  $30^\circ$ . Yeast spores contain volutin. Comparative measurements on the glycogen, fat and volutin content of fungi show that glycogen content rises quicker than volutin and falls quicker. The formation and disappearance of glycogen and volutin are dependent on external factors. The fat content increases less quickly and remains even in very old cells. Large supplies of N increase the formation of all 3 substances, but volutin most. Volutin apparently is not related to the formation of the nucleus. Volutin is a protein probably related to the nucleoproteins because it contains P and nucleic bases.

JULIAN H. LEWIS

Factors influencing development of metachromatic granules in the diphtheria bacillus. EMERSON MEGRAIL. *J. Infectious Diseases* 31, 393-401(1922).—J. H. L.

Food accessory factors (vitamins) in bacterial growth. Observations on the ultimate source of accessory growth substances for yeast. VII. R. C. ROBERTSON AND D. J. DAVIS. *J. Infectious Diseases* 32, 153-8(1923).—Yeast is incapable of synthesizing its own "growth-stimulating" substance or substances on a synthetic medium. Beef heart, carrot, potato and yeast cells contain a  $H_2O$ -sol. substance or substances which when added to this synthetic medium in high dilns. permit the luxurious and continued growth of yeast. In the concns. in which these exts. were used they alone will not permit continued growth. These, or similar growth-stimulating substances, seem therefore essential to the continued growth of yeast. Their ultimate origin is as yet unknown. The luxuriance and duration of the growth of yeast on mediums which do not permit its continued growth are roughly proportional to the no. of cells used for the original inoculation. It is also somewhat proportional to the length of time elapsing between the original inoculation and subsequent inoculations to successive transplants.

Yeast cells, to a large extent, possess the power of "taking over" these essential food substances when present in small amts. in the medium and utilizing them in further growth. A suspension of killed, washed yeast cells plus the proper amt. of inorg. salts forms a suitable medium for the continued growth of yeast. JULIAN H. LEWIS

**The influence of carbon dioxide on the growth of bacteria.** G. E. ROCKWELL. *J. Infectious Diseases* 32, 98-104(1923).—When all O and CO<sub>2</sub> was removed (even the CO<sub>2</sub> produced by the bacteria) growth was prevented of *B. subtilis*, a saprophytic tubercle bacillus, a staphylococcus, *B. proteus*, *B. welchii*, an anaerobe from a steer hide, a streptococcus, a pneumococcus, and a meningococcus; but when only O was removed and CO<sub>2</sub> was added, growth occurred in all instances. The growth of bacteria under pyrogallic acid and alkali was interfered with when too much alkali was added, probably due to the absorption of all CO<sub>2</sub> as formed. This is further substantiated by the parallel expts. under a stream of N. A streptococcus when first cultivated from the host required the presence of CO<sub>2</sub> and could not stand any appreciable amt. of O. But a pneumococcus and meningococcus when 1st cultivated from the host required CO<sub>2</sub>, but could stand a fairly large amt. of O. These facts again prove that many bacteria when 1st cultivated from the host need CO<sub>2</sub> for rapid growth, and that some of these cannot stand a concn. of O.

JULIAN H. LEWIS

**A safe method for securing anaerobiosis with hydrogen.** IX. A. C. RICHARDSON AND C. C. DOZLER. *J. Infectious Diseases* 32, 617-21(1922).—Anaerobiosis is produced in a specially constructed and equipped jar. This jar is completely evacuated with an efficient vacuum pump and then filled with H<sub>2</sub>. The remaining O is removed by means of a catalyzer which consists of a nichrome coil activated by an elec. current. The feature of this app. and method which is emphasized is the small risk of explosion from ignition of the N<sub>2</sub>.

JULIAN H. LEWIS

**Reaction of the medium and the production of diphtheria toxin.** G. ART AND G. LOISEAU. *Ann. inst. Pasteur* 36, 535-61(1922).—The first essential in the production of an active diphtheria toxin is a nutritive medium supporting rapid growth. The medium of Martin, adjusted to pH 7.5-7.9, gives regular results, furnishing a toxin of such strength that 1/700 cc. kills a 350 g. guinea pig in 4 days. At reactions more alk. than pH 8.6 toxin does not seem to be formed. Its activity lessens rapidly when the reaction is more acid than 6.8. With an initial reaction of 5.8-6.1 it takes 0.1 cc. of the product to kill a guinea pig in 4 days. Alky. and acidity are both unfavorable to the preservation of the toxin. The progress of reaction in the course of growth is such that media initially alk. become less alk., and initially acid become less acid. E. R. LONG

**Immune reactions toward a new, artificially produced race of *B. coli*.** PAUL FABRY. *Ann. inst. Pasteur* 36, 654-63(1922).—*B. coli communior* loses the power to produce indole in peptone water if increasing quantities of phenol up to 0.2% are added daily to the culture medium. The modification is inherited even in media contg. no phenol. Injection of this new *B. coli* into animals provokes the formation of agglutinins which are rigorously sp. for the modified *B. coli*. The new *B. coli* is, however, still agglutinated by ordinary anticoli serum. E. R. LONG

**Observations on a mycologic method for the identification of certain sugars and other carbohydrates.** ALDO CASTELLANI AND F. E. TAYLOR. *Ann. inst. Pasteur* 36, 789-804(1922).—A biol. method, much simpler and more rapid than chem. methods, is proposed for the identification of sugars. Tubes contg. 1% of the sugar to be identified dissolved in sterile peptone water are seeded with certain hyphomycetes. *Levalose* is identified by its susceptibility to the action of *Monilia krusei* Castellani and failure to be attacked by *Monilia batanica* Castellani. Maltose is fermented by *Monilia pinoyi*, but not by *Monilia krusei*; galactose is fermented by *Monilia metalondniensis* but not by *Monilia pinoyi* and by *Monilia tropicalis* but not by *Monilia bronchialis*;

lactose is fermented by *Monilia pseudotropicalis* but not by *Monilia macedoniensis*; sucrose is fermented by *Monilia tropicalis*, but fails to reduce Fehling soln.; inulin is fermented by *Monilia macedoniensis* but not by *Monilia rhoi*. The method can be employed in the identification of sugar in urine. Urine is divided in sterile tubes, which are seeded, resp., with *Monilia krusei*, *M. pinoyi*, *M. metalondinensis*, *B. paratyphosis* and *B. coli* and gas production is noted. If but a single sugar is present its identification on the basis of fermentation can be made.

E. R. LONG

**A selective culture medium for the diphtheria bacillus.** E. A. GREENSPON. *Bull. Johns Hopkins Hosp.* 34, 30-3(1923).—A serum medium is described which is adjusted to a  $p_H$  of 6.4 with citric acid. This acid has a differential effect in inhibiting the growth of many of the common throat organisms and has a growth-accelerating effect on *B. diphtheriae* to which it apparently serves as a source of C. The medium is definitely superior to Loeffler's serum for the cultivation and isolation of the diphtheria bacillus.

A. P. LOTHROP

**Studies on the action of electrolytes on bacteria. II. The influence of the trivalent positive salts on the rate of migration of bacteria in an electric field, and their effects on growth and virulence of pathogenic organisms.** C. SHEARER. *J. Hyg.* 12, 77-86(1922).—Evidence shows that bacteria in spleen broth or neutral Ringer soln. carry a negative charge and move to the anode in an elec. field. The addn. of a trace of positive tervalent ion such as La, Ce, or Yb lessens or neutralizes this charge. With sufficient amts. the charge disappears and the bacteria agglutinate. Living bacteria seem more sensitive to the action of these ions than non-living colloidal particles. The addn. of negative tervalent ions is without effect.

JOHN T. MYERS

**Behavior of diphtheria bacilli in acidified media, especially with reference to virulence tests.** I. WALKER HALL. *J. Hyg.* 12, 155-67(1922).—The growth of diphtheria bacilli in sugar-free casein digest broth may be accelerated by the addn. of dil. nitric, acetic, and lactic acids and delayed by certain monobasic fatty acids. The limiting acid zone for toxic and non-toxic strains is unaffected by the initial acidification with several acids, but increased by citric acid. Toxic strains produce earlier and more progressive alky. when 0.005 *N* acetic or nitric acid is in the medium. Butyric, formic and propionic acids have the opposite effect.

JOHN T. MYERS

**The growth and respiration of sulfur-oxidizing bacteria.** S. A. WAKSMAN AND R. L. STARKEY. *J. Gen. Physiol.* 5, 285-310(1923).—*Sulfomonas thiooxidans* oxidizes S and  $Na_2S_2O_3$  completely to  $SO_4$ . Other S-oxidizing bacilli either produce S from  $S_2O_3$  or convert it to  $SO_4$  or persulfate. Its C is derived from atm.  $CO_2$ ; it is incapable of deriving C from carbonates or org. matter. The ratio between the S oxidized and the C assimilated from the atm. is with S, 31.8 and with  $S_2O_3$ , 64.2. The higher  $S_2O_3$  ratio is due to the smaller amt. of energy liberated. Only 6.65% of the energy available in the oxidation of S to  $H_2SO_4$  is used to reduce atm.  $CO_2$  and to assimilate C. The  $SO_4$  radical has no injurious effects on S oxidation. Nitrates are injurious to growth and respiration. A definite correlation exists between the amt. of S present and the velocity of oxidation; max. oxidation is reached at a concn. of 25 g. S in 100 cc. of medium. Larger amts. of S are not injurious. Glucose at less than 5% concns. is not injurious and has no appreciable influence upon S oxidation or C assimilation. Peptone almost stops S oxidation at a concn. of 1% and even 0.1% concns. are injurious. This organism can withstand large amts. of  $H_2SO_4$ ; at an initial concn. of 0.25 *M*, S oxidation is but slightly subnormal. 1.5 *M* acid may be withstood without destruction. The optimum  $p_H$  for growth is from 2.0 to 5.5, dropping rapidly on the alk. side. A method of studying respiration in terms of S oxidation is given.

CHAS. H. RICHARDSON

## D—BOTANY

B. M. DUGGAR

**Effect of different reactions on the growth and nodule formation of soy beans.** O. C. BRYAN. *Soil Science* 13, 271-302(1922).—The effect of variation of  $p_H$  from 3 to 10 upon the growth and inoculation of soy beans in both soln. and sand cultures is reported. Shive's nutrient soln. was found favorable for growth and inoculation of soy beans in sand cultures but not in soln. cultures. Crone's nutrient soln. proved satisfactory in both. Variations in  $p_H$  were obtained by adding graded amts. of  $H_2SO_4$  and  $Na_2CO_3$ . To keep variation in  $p_H$  due to growing plant at a minimum, solns. were renewed daily. The most favorable reaction for growth and inoculation of soy beans was  $p_H$  6.5. The limits for inoculation were from  $p_H$  4.6 to 8. The limits for growth were  $p_H$  3.9 to 9.6. Reactions 4.95 and 8.2 are injurious to the growth but did not entirely prevent inoculation. Different strains of bacteria showed slight differences in critical  $p_H$ .  
RICHARD BRADFELD

**The anabolism and katabolism of asparagine in plants.** D. PRIANISCHNIKOV. *Ber. botan. Ges.* 40, 242-8(1922).—Expts. were undertaken on *Cucurbita Pepo* and *Vicia sativa* with  $NH_4Cl$  or  $(NH_4)_2SO_4$  alone and plus  $CaCO_3$ . Total N, protein N, asparagine N, and  $NH_3$  were detd. in 100 plants. The effect of glucose was to increase the asparagine N and decrease the  $NH_3$  N in the plants. Asparagine plays the same role in plants as urea does in animal metabolism.  $NH_3$  is the first and last step in the N metabolism of such green plants and asparagine is the intermediate product.  
F. C. COOK

**Poisonous properties of *Bikukulla cucullaria* (Dutchman's Breeches) and *B. canadensis* (Squirrel-corn).** O. F. BLACK, W. W. EGGLESTON, J. W. KELLY AND H. C. TURNER. *J. Agr. Research* 23, 69-78(1923).—Tops and roots of *Bikukulla cucullaria* and the roots of *B. canadensis* were used. The plants were collected just previous to the flowering stage in 1921 in Va. Three alkaloids were detd. and the min. fatal doses to mice of 20 g. wt. were found to be 0.02 g. per kg. of body wt. for the 2 alkaloids from *cucullaria* and 0.40 g. per kg. body wt. for the alkaloid in *canadensis* roots. Feeding expts. using steers (conducted by the Va. Expt. Sta.) showed that *B. cucullaria* was toxic. An alkaloid named cucullarine was found in *B. cucullaria*. Its properties are described. This alkaloid probably occurs in *B. canadensis* also, judging from its physiol. effects on mice.  
F. C. COOK

**Effect of various inorganic nitrogen compounds, applied at different stages of growth on the yield, composition and quality of wheat.** JERHRL DAVIDSON AND J. A. LE CLERC. *J. Agr. Research* 23, 55-68(1923); cf. *C. A.* 17, 444.—Expts. were carried out on hard winter wheat in Nebraska where the prevalence of typical yellow berry fluctuates from year to year. The effects of  $NaNO_3$  and other N compds. were detd., when applied at the rate of 320 lbs. of  $NaNO_3$  per acre. The chemicals were applied in soln. and 25 gals. of  $H_2O$  used for each application. The total yield and the % of grain are recorded for plots to which the chemicals were applied at various stages of growth. The first stage was when the crop was 2" high; the 2nd stage was at the time of heading and the 3rd stage was the milk stage. The % of yellow berry, the wt. per bu. and wt. per 1000 kernels of wheat are given. No correlation was found between protein content and the wts. The % of protein and  $P_2O_5$  are recorded. The lack of correlation between the N and  $P_2O_5$  contents of wheat grown at Arlington, Va., on plots to which various chemicals were applied, was noted. The % of ash and  $SiO_2$  in straw from plots to which chemicals were applied at the 3 stages are recorded. The application of N in any of the inorg. forms in the early stages of growth produced the high-



est yields of wheat. At the time of heading the application of the inorg. forms of N produced the best quality of grain with reference to yellow berry and protein content. A high protein content of the straw was also produced. No difference in the effect of the different forms of inorg. N was observed. The non-nitrogenous chemicals produced no effect on yield or on the quality of grain. These included KCl, NaOH,  $\text{H}_2\text{SO}_4$ , KOH,  $\text{H}_2\text{O}$ , NaCl,  $\text{CaCl}_2$ , HCl,  $\text{K}_2\text{SO}_4$ , and  $\text{MgCl}_2$ . The application of N at the 1st 2 stages caused a depression of the  $\text{P}_2\text{O}_5$  content in the grain and straw and a marked depression of the ash and  $\text{SiO}_2$  contents of the straw. F. C. COOK

**Respiration of apple seeds.** G. T. HARRINGTON. *J. Agr. Research* 23, 117-30 (1923).—The manometric respiration app. (cf. C. A. 17, 1257) were used to test Newtown Pippin seeds. The respiratory intensity of the dormant seed was low. It increased with advancing germination and with a rise of temp., causing an impoverishment of easily oxidizable substances. At decreased temps. the respiratory quotient decreased and probably leads to an increase of acids and sugars. Correlated with a relatively high rate of oxidation at high temp. is a tendency for the seeds to become more dormant. The quotient becomes low with advancing germination, indicating the rapid transformation of fats and the accumulation of sugar. Temp. coeffs. are different at different steps in the oxidative processes which constitute respiration and these differences are related to the different temp. effects upon the physiol. condition of the living embryo. To gain an understanding of respiratory processes it is necessary to study  $\text{O}_2$  consumption and  $\text{CO}_2$  production in their relations to each other. F. C. COOK

**After-ripening and germination of apple seeds.** G. T. HARRINGTON AND B. C. HITE. *J. Agr. Research* 23, 153-61 (1923).—Seeds from apples of several varieties, some having been held in cold storage, were studied. A good supply of  $\text{O}_2$  seems to be present within apples held at low temp. The other conclusions are not of chem. interest. F. C. COOK

**The histology of certain orchids with reference to mucilage secretion and crystal formation.** EDNA L. SMITH. *Bull. Torrey botan. Club* 50, 1-16 (1923).—Paraffin sections of the mucilage and raphides of young buds and mature flowers were stained and the crystals in certain cells were counted. The functions of these are discussed. F. C. COOK

**Structure, physical characteristics, and composition of the pericarp and integument of Johnson grass seed in relation to its physiology.** G. T. HARRINGTON AND WM. CROCKER. *J. Agr. Research* 23, 193-222 (1923); illus.—Measurements in microns of the coat structures of Johnson grass and Sudan grass caryopses are recorded. Microchem. tests show that the cells of the aleurone layer of Johnson grass caryopses consist of hemicellulose, the inner integument cell walls contain suberin impregnated with fatty substances in the inner cells and little suberin and some cellulose in the outer cell walls. The pericarp cells contain pectic substances and are suberized; a little Ca, cellulose and Fe are present in the outer layer. All layers swell in 2% oxalic acid and in dil.  $\text{NH}_4\text{OH}$ . Bleaching tests using Javelle  $\text{H}_2\text{O}$  are recorded. The resistance of coat structures to the action of 50% chromic acid was detd. The resistance of the coat structures to I penetration was somewhat greater than for Sudan grass and much greater than for wheat and corn. Immersion for 7 days in molar soln. of KCNS, NaCNS or  $\text{LiNO}_3$  killed all the caryopses; nearly all were killed with  $\text{KNO}_3$ ,  $\text{NaClO}_3$ ,  $\text{Ba}(\text{CNS})_2$  and  $\text{CO}(\text{NH}_2)_2$ ; about 50% survived after immersion for 7 days in  $\text{Li}_2\text{SO}_4$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ . Immersion of fully after-ripened caryopses for 1 or 2 days in 5%  $\text{CH}_3\text{COOH}$ , 5% HCl, 5%  $\text{NH}_4\text{OH}$ , 3% alc. KOH, 95% EtOH, acetone,  $\text{Et}_2\text{O}$ ,  $\text{CHCl}_3$  or xylene killed all the caryopses. Immersion for 1 day in 3%  $\text{H}_2\text{SO}_4$  killed 80% and for 2 days in soln. of  $\text{CaCl}_2$  killed 20%. The controls in  $\text{H}_2\text{O}$  were uninjured. All of the above-mentioned solvents or solutes increased the subsequent rate of bleaching of the thoroughly

washed caryopses with Javelle  $H_2O$ , and the rate of penetration of I soln. Hydrates had the same effect, fat solvents next, followed by acids and  $CaCl_2$ , which had little effect. The markedly dormant characteristics of Johnson grass seed are described and comparisons made with the closely related Sudan grass seed which germinates freely.

F. C. COOK

**Alcohol and the numerical proportion of the sexes in a declinuous plant (*Melandrium*).** C. CORRIENS. *Naturwissenschaften* 10, 1049-52(1922).—A study of the effect of EtOH on the pollen and the fertilization of *Melandrium*. Assuming with Bluhm (cf. *Sitzb. preuss. Akad. Wiss.* 1921, 549-56) that there are male and female determinative germs, a greater resistance of the male than the female determinative pollen to EtOH vapor was found, corresponding to the greater vitality to aging of the male determinative pollen. The % of total fertile pollen was also decreased to 1/3-1/6 by exposure to EtOH for 1 hr. The results were analogous to those obtained by Bluhm for mice (*loc. cit.*).

C. C. DAVIS

**The stimulation of cell functions and its agricultural importance.** METHODOR POPOFF. *Naturwissenschaften* 10, 1128-9(1922).—More data are given in continuation of earlier expts., many references to which are listed. Treatment of plant seeds with  $MgCl_2$ ,  $MgSO_4$ ,  $MgCl_2 + Mg(NO_3)_2$ ,  $MgCl_2 + MnCl_2$  and  $MgSO_4 + MnSO_4$  stimulated them so that they developed seedlings 1.5-2 times larger and heavier, and gave a yield averaging 40-50% and in some cases 70-100% higher than normal. By a combination of these salts with subsequent short treatment with  $Et_2O$  vapor or addn. of  $Et_2O$  to the salt solns. the seeds were stimulated still more. Treatment with the salts varied from 1 to 12 hrs., depending on the hull. Considerable stimulation was effected by  $Et_2O$  vapor alone. It is suggested that these principles be applied to agriculture. C. C. D.

**Anatomical and chemical studies of the sand spur (*Cenchrus tribuloides* L.).** H. W. YOUNGKEN AND C. H. LA WALL. *Am. J. Pharm.* 94, 567-83(1922).—Ash averaged 3.95% of which 10% was Si; the balance is made up of compds. of K, Ca, Mn and Fe. The water-sol. ext. was 3.55%, of which 0.55% was reducing sugars, the balance being mucilaginous in character. Alkaloids, glucosides, starch and tannin were not found. An aldehyde was detected but not identified. Alc. ext. was 3.17%, mainly chlorophyll and resinous and oily constituents; no alkaloids or glucosides. Petroleum-ether ext. was 2%, principally fat.  $Et_2O$  ext. was 3.3%; acid no. of ether ext. was 19.10, sapon. no. 197, and I no. 60.

W. G. GAESSLER

**The toxic constituent of greasewood (*Sarcobatus vermiculatus*).** J. F. COUCH. *Am. J. Pharm.* 94, 631-41(1922).—Large quantities of K and Na oxalates were found. These are responsible for range poisoning. Toxic alkaloids, glucosides, and saponins are present. HCN or its compds. was not found.

W. G. GAESSLER

**The plant albumin "Leucosin."** H. LÜERS AND M. LANDAUER. *Biochem. Z.* 133, 598-602(1922).—Leucosin was prepd. from barley according to the method of Osborne with distd.  $H_2O$  instead of NaCl soln. The hydrolysis of a small sample gave results closely approximating those reported by Van Slyke.

F. S. HAMMETT

**Correction: "The identity of hordein and bynin."** H. LÜERS. *Biochem. Z.* 133, 603-4(1922); cf. *C. A.* 14, 950.—In the formula for calcn. of histidine 1.5 D should be used instead of 1.667 D.

F. S. HAMMETT

**Proof of Treub's hypothesis.** L. ROSENTHALER. *Biochem. Z.* 134, 215-24 (1922).—Treub's hypothesis is that HCN is the 1st recognizable product of N assimilation in plants and that it is the building stone of plant proteins (cf. *Ann. d. jard. bot. d. Buitenzorg.* 13, 1(1896)). R. found HCN in traces in 56 of the 88 types of plants studied. The administration of tyrosine to *Sorghum nigrum* was followed by the appearance of HCN in the plant. Hence Treub's hypothesis for this plant is insufficient. F. S. H.

**Enzymes of the latex of the Indian poppy (*Papaver somniferum*).** H. E. ANNETT. *Biochem. J.* **16**, 765-9(1922).—The darkening of the latex of the Indian opium poppy is due to oxidation. Strangely enough, guaiacum, benzidine and tyrosine are oxidized by the latex in the absence of  $H_2O_2$ , and "in almost all the expts. tried  $H_2O_2$  inhibited these reactions."

BENJAMIN HARROW

**The effect of ultra-violet light, radium and X-rays on plant diseases.** FRIEDR. PICHLER AND ARTUR WÖBER. *Centr. Bakt. Parasitenk., II Abt.* **57**, 319-27(1922).—X-rays and ultra-violet light give good results in treating diseases of plants. Acid sprays that contain free O or form O enhance the action. X-rays are more efficient than ultra-violet rays. Ra had no action on the diseases investigated. J. H. LEWIS

**The nature of the carbohydrates in the leaf, stem and tuber of *Amorphophallus konjaku* and their variations in amount under different conditions.** KIKO GORO. *J. Biochem. (Japan)* **1**, 201-11(1922).—The fresh material was invariably used for the analyses; the method of examn. is given in detail. The glucose equiv. detd. as before and multiplied by 0.9546 gave the amt. of mannan. The carbohydrate compn. of the tuber during the resting period (5-year old tuber removed from ground in Oct. and stored in dry sand for 2 months before analysis) and at a very early stage of growth (when plant was 10-15 cm. high) is resp., mannan 58.80, 54.88; starch 18.85, 16.37; glucose 0.57, 1.78; fructose 1.20, 1.19. Complete analyses are further given of the carbohydrate compn. of leaves, stalk, new tuber, and old tuber during the normal assimilating period of the growing plant kept both in the light and dark. The general conclusion is that the content of sugars in the leaves in full functional activity is markedly higher than in others; this is evidently associated with the process of assimilation; and the first sugar to arise in photosynthesis must therefore be glucose or fructose but not mannose. Glucose and fructose occur everywhere in almost similar proportions but there is no sucrose, which is the important circulating sugar in higher plants. Here sugars travelling in the tissues are glucose and fructose, and this is supported by the fact that under normal and exptl. conditions the relative amts. of both remain const. S. M.

**Influence of formalin on the higher plants.** E. NICOLAS AND G. NICOLAS. *Compt. rend.* **175**, 1437-9(1922).—Beans grown in Knop soln. as control and Knop soln. contg. 0.321 g. per l. of formalin gave 1.37 and 1.29 g. of roots, resp., and 4.74 and 6.48 g. of tops. With 0.808 g. of formalin per l., beans grown during the same period yielded 0.62 g. of roots and 4.77 g. of tops. Where there is an insufficiency of chlorophyll, HCHO exercises a toxic action. As soon as the chlorophyll can play its role of a catalyzer the action of HCHO is favorable, at least up to the concn. of 0.321 g. of formalin per l.

L. W. RIGGS

**Nature and function of the reticular apparatus of Golgi.** MANUEL SÁNCHEZ Y SÁNCHEZ. *Compt. rend.* **175**, 1439-40(1922).—This study was histological using the epidermis of the bean seed *Faba vulgaris*. The process of oxidation in the cell appears to bear a relation to the development of the reticular app. of Golgi, whereupon it is conjectured that certain enzymes are produced in the reticule, which are indispensable to the nutrition and development of the cells.

L. W. RIGGS

**Genesis of carbohydrates in wheat. Presence of levulosans in the stalk.** H. COLIN AND H. BELVAL. *Compt. rend.* **175**, 1441-3(1922).—The only carbohydrates contained in the wheat leaves are sucrose and its products of hydrolysis. The stalk before heading out contains only those carbohydrates received from the leaves and during this period the ratio of reducing sugar to sucrose is much larger in the stalk than in the leaves. Starch, dextrin and maltose are absent from the stalk. At the beginning of forming the head a marked change occurs in the stalk. Although the proportion of sucrose increases continuously the rotatory power changes from + to — and at the same time hydrolysis by acids yields increasing amts. of levulose. Thus the ratio of

dextrose to levulose, which in May was 1.48, falls to 0.28 by July 1. The total sugar ranged from 1.9 g. per 100 g. of fresh leaves on May 18 to 3.35 g. on July 1, upper half of stalks 1.57 to 8.1, lower half of stalks 3.4 to 8.74. Reducing sugars in leaves 0.49 to 0.73, upper half of stalks 0.79 May 18 to 2.33 May 29 to 0.81 July 1, lower half of stalks 1.52, 2.31 and 1.20 on the same dates. The non-reducing carbohydrates in wheat stalks at maturity are sucrose and levosin or some levulosan analog. L. W. RIGGS

**Protein precipitation in grasses.** MARGARET H. O'DWYER. *Proc. Linnæan Soc. N. S. Wales* 47, 513-5(1922).—A comparison is made of the pptn. of proteins by Stützer's reagent (A.O.A.C. Methods of Analysis, 1921), tannin-salt soln. (10% tannin and 10% NaCl), 94% alc., and Barnstein's method (Technical Methods of Chemical Analysis, Lunge & Keane, 1911, p. 449). Results on Australian grasses appear to bear out Petrie's contention (*Proc. Linnæan Soc. N. S. Wales* 33, 837(1908)) that Stützer's reagent ppts. some of the non-protein N. (Cf. Chibnall and Schryver, *C. A.* 15, 2467; Buston and Schryver, *C. A.* 16, 728.) A. P. COUTURE

**Origin and structure of plant galls.** M. T. COOK. *Science* 57, 6-14(1923).—Principally a review and discussion. L. W. RIGGS

## E—NUTRITION

PHILIP B. HAWK

### NORMAL

**The influence of aliphatic esters upon nitrogen secretion.** U. G. BYLSMA. *Nederland. Tijdschr. Geneeskunde* 65, II, 788(1921).—100 mg. Et or Am acetate, *per os*. increased the N secretion of a dog of 7 kg. to 11.5%. R. BEUTNER

**Fermented beverages and the new theories of nutrition.** L. RANDOIN AND P. PORTIER. *Rev. vit.* 57, 277-84(1922).—Largely a general discussion of the nutritive value of fermented beverages. Guinea pigs and pigeons in advanced stages of polyneuritis were rapidly cured by the administration of small doses of ordinary red and white wines. P. R. DAWSON

**The effect of change of temperature on the basal metabolism of swine.** J. W. CAPSTICK AND T. B. WOOD. *J. Agr. Sci.* 12, 257-68(1922). R. B. DEHMER

**Potato meal as a source of nourishment for small children.** ERICH MÜLLER. *Klin. Wochschr.* 1, 2378-80(1922).—Potato meal can be used in the compounding of artificial foods for small children. In some cases its ingestion is followed by a slight laxative action which is, however, transitory. The urine is usually alk. The meal is rich in inorg. salts and contains proteins that are almost as easily utilizable as those of milk and far more easily utilizable than those of wheat. Potato meal is cheaper than wheat meal. MILTON HANKE

**The protein-conserving action of urea.** W. VOLTZ AND HANSEN. *Mitt. deut. Landw.-ges.* 37, 647-8(1922).—Urea may be used as a protein carrier to a certain extent in the rations of lambs and milk cows without harmful results. It appears to have a beneficial action if it is used at the rate of about 150 g. per day per cow and is mixed with sufficient carbohydrate-carrying food. K. D. JACOB

**The storage of vitamin A in the liver of the rat.** KATHERINE H. COWARD, JOAN L. LUSH AND M. GRACE PALMER. *Lancet* 1923, I, 124-5.—The concn. of vitamin A in the liver of the rat varies with the concn. of this substance in the diet. On being deprived of vitamin A the rat ceases to grow apparently before the store of vitamin in the liver is exhausted. Apparently a reserve is necessary for some function of the animal body other than growth. E. R. LONG

**The adequacy of certain synthetic diets for the nutrition of pigeons.** KANEMATSU SUGIURA AND S. R. BENEDICT. *J. Biol. Chem.* 55, 33-44(1923).—"A synthetic diet

consisting of casein 22, cane sugar 10, starch 27, agar-agar 2, salt mixt. 3, butter fat 30 and yeasts 6%; or a synthetic diet contg. casein 22, cane sugar 10, starch 37, agar-agar 2, salt mixt. 3, yeast 6, and lard 20% is an adequate diet for fertile egg production, growth, and maintenance of common pigeons. Daily rations of from 15 to 20 g. of these synthetic diets are sufficient to promote normal growth in squabs. If a diet contains proper proportions but supplies too few cal., pigeons upon that diet may not maintain their normal wt. and do not lay eggs. Pigeons on a diet of sufficient cal. value, even though the diet lacks fat and fat-sol. vitamin, may maintain excellent condition, and may produce fertile eggs and rear healthy squabs. Hence fat-sol. vitamin is not essential in any stage of avian nutrition. An adequate food for pigeons should contain about 70 cal. in the daily ration. From the fact that the diets employed contain no antiscorbutic vitamin it is safe to say that the pigeon requires no antiscorbutic vitamin. Common pigeons can be raised normally under strictly lab. conditions and may, therefore, render service for the study of nutritional problems."

A. P. LOTHROP

**Potassium in animal nutrition. I. Influence of potassium on urinary sodium and chlorine excretion.** H. G. MILLER. *J. Biol. Chem.* 55, 45-59(1923).—A sudden increase of K salts in the diet causes an immediate increase in the Na and Cl excretion in the urine of pigs during the following 24 hr. period. The av. daily excretion for the 4 day period after the introduction of  $K_2HPO_4$  in the food was approx. the same as during the 4 days preceding the administration of the  $K_2HPO_4$ . If the high K intake is continued there is a decrease in the Na and Cl excretion and as the high K period is prolonged a stage is reached where a considerable portion of the ingested NaCl does not appear in the urine. This result cannot be attributed to any interference of the K with the absorption of the Na. The amt. of K taken into the blood at any one time does not det. how much Na and Cl will be found in the urine as the total excretion remained practically unchanged when an increase of 50% was made in the amt. of  $K_2HPO_4$  ingested. Thus the animal is able to control its Na and Cl excretion and can distribute these elements as required by the different parts of the body during the absorption of large amts. of K, which may at other times cause increased Na and Cl excretion.

**II. Potassium in its relation to the growth of young rats.** *Ibid* 61-78.—The growth of rats can be greatly retarded by reducing the K content of the ration below approx. 0.1% but no other distinct physiol. abnormality appears as a result of this nutritive deficiency. Response to increased K in the diet seems to depend at what growth stage the  $K_2HPO_4$  is given. Response was obtained with one group of rats during the 4th week but 2 other groups did not respond when either  $K_2HPO_4$  or KCl was added to the diet during the 11th week. The response obtained at the end of the 4th week was not permanently successful as cessation of growth finally took place followed by death. Inadequate K during the early development of the organism may not only prevent the growth of body tissue but causes abnormal physiol. changes which result in the appearance of harmful symptoms later such as edema of the eyes and respiratory trouble. These disturbances did not appear during the period of low K intake but only when K was given later. Normal growth was not obtained by substituting Na for K and this failure does not support the view (Osborne and Mendel, *C. A.* 12, 1810) that Na may replace K in the physiol. functions that it performs in the phenomenon of growth. No ill effects were produced by a ration in which the ratio of K to Na was 14:1 and the normal K and Na content of the blood was not altered by feeding a ration high in K. A. P. I.

**Reproduction on "synthetic" diets when purified agar is added to the mixture.** H. S. MITCHELL. *Am. J. Physiol.* 62, 557-8(1922).—The standard casein diet used by Osborne and Mendel, consisting of casein 18, starch 51, salt mixt. 4, butter fat 9 and Crisco 18% + 0.4 g. dried yeast daily, produces excellent growth in white rats, but fails to secure reproduction. The replacement of 5% of the starch by an equal amt. of agar

was followed by successful reproduction. M. considers that the defect in the standard casein diet is in the lack of bulk or roughage which is supplied by the agar. J. F. L.

**Basal metabolism in the diagnosis of thyroideal syndromes.** MARCEL LABBÉ. *Bull. soc. hyg. aliment.* 10, 625-7(1922).—Brief outline of the advantages of applying the measurement of basal metabolism to the study of thyroideal syndromes, more particularly in Basedow's disease, and for following the results of treatment. A. P.-C.

#### ABNORMAL

**The antiscorbutic vitamin in some Oriental fruits and vegetables.** H. EMBREY. *Philippine J. Sci.* 22, 77-82(1923).—Ten g. daily of pomelo, cucumber, chico and guava protected guinea pigs from scurvy for 9 wks., while 15 g. daily of banana, kangkong leaves, and kamote leaves were essential for similar protection. Incomplete expts. with lansones indicated that 10 g. daily were evidently insufficient as a protection from scurvy. H. B. LEWIS

#### F—PHYSIOLOGY

##### ANDREW HUNTER

**Contribution to the physiology of the cerebrospinal fluid.** HENRIJEAN AND SCHOOF. *Bull. acad. roy. med. Belg.* [5] 2, 353-8(1922).—The nervous system is protected by an impermeable membrane. The cerebrospinal fluid, enclosed within this membrane, has therefore, an invariable compn. After administering drugs, contg. As or I, in cases of lues, etc., not the slightest trace of these elements is found in the cerebrospinal fluid, obtained by lumbar puncture, although the drugs are present, of course, in the blood. Some examns. on clinical cases, confirming this fact, are cited. With some very progressed pathological changes this impermeability no longer exists. R. BEUTNER

**Demonstration of microscopic preparations of muscle tissue and of the electric organ of the thornback, treated with the potassium reagent of Macallum.** M. W. WOERDEMAN. *Nederland. Tijdschr. Geneeskunde* 65, II, 779(1921).—W. confirms the statement of Macallum that the K compds. are localized exclusively in the anisotropic layers of the muscle tissue. In the elec. organ the so-called elec. plates contain much K; the surrounding connective tissue contains little of it. R. BEUTNER

**The influence of the innervation on the creatine content of muscle.** G. D. COHEN-TERVAERT AND J. G. DUSSER DE BARENNE. *Nederland. Tijdschr. Geneeskunde* 66, I, 2303-4(1922).—Muscles of decerebrated animals which are subject to a continuous hyper-innervation are also subject to regular movements produced artificially by elec. irritation of the homolateral and the contralateral *nerus peroneus*. The creatinine content of these muscles is compared with the creatinine content of normal muscles. While the continuous hyper-innervation, as such, does not produce an increased creatinine content, it does increase it if combined with artificial regular movements, as described. R. BEUTNER

**Physiology of the blood vessels.** I, II. G. VERNONI. *Arch. fisiol.* 19, 123-62 (1921); *Physiol. Abstracts* 6, 501.—Rabbit or horse serum favors the contractions of rings of calf arteries due to adrenaline, BaCl<sub>2</sub>, and nicotine. The action is immediate. Ox pericardial fluid has a favorable but almost instantaneous influence on contractions due to elec. stimuli when applied on the internal surface of the artery, but has no action when applied on the external surface. Adrenaline likewise has a contracting action only when applied on the intima. BaCl<sub>2</sub> causes arterial contractions when applied on either surface, but applied internally the contractions occur immediately, while applied externally they begin gradually. In contractions due to adrenaline and

BaCl<sub>2</sub> or pericardial fluid has about the same effect as blood serum. The flow of a fluid within a blood vessel has an inhibitory influence on contractions due to elec. stimuli; this is maximal when Ringer's soln. is used, minimal for pericardial fluid. A sudden distension of an artery increases its elec. excitability; but this is a little modified by a gradual increase of the intravascular pressure. From a physiol. point of view the intima and media of blood vessels form one unit. H. G.

**Thyroid and fluid exchange.** Observations on intravenous saline and oral water administration in rabbits before and after thyroidectomy. H. SCHAAAL. *Biochem. Z.* 132, 295-308(1922).—No alterations in the course of the NaCl and dry matter changes of the blood in diuresis induced by intravenous injection of NaCl solns. were obtained by thyroid feeding or removal. The diuresis induced by oral ingestion of H<sub>2</sub>O was affected similarly in rabbits as in dogs as found by Eppinger (Zür pathol. u. Therap. des Menschl. Oedema, Springer, 1917) after thyroid feeding or removal. The influence of the diet, particularly the drinking, is so strong that previously "desiccated" animals show a different course of fluid exchange from the normal. Hemoglobin, as a measure of H<sub>2</sub>O content, is only of value in severe experimentation such as blood-letting. It is concluded that the thyroid is only effective in H<sub>2</sub>O exchange and diuresis when its tissue activity is concerned. If alteration in swelling pressure of protein has to do with the fluid exchange through mediation of the thyroid, it is accomplished primarily through tissue action. The action of the thyroid on the blood protein is apparently not sufficient to influence fluid exchange in the living animal. F. S. HAMMETT

**Concerning urea excretion in human urine.** A. LUBLIN. *Biochem. Z.* 133, 21-3(1922).—Polemical reply to György and Stenström (C. A. 16, 1979). F. S. H.

**The dependence of calcium ionization on the amount of bicarbonate in physiological salt solution and serum.** H. MAIWEG. *Biochem. Z.* 134, 301-7(1922).—The frog heart was used as the test object. The dependence of the Ca-ion concn. on the bicarbonate concn. is not expressed by the formula of Hamburger and Brinkman (*Biochem. Z.* 88, 97(1918)). The influence of a change in the HCO<sub>3</sub><sup>-</sup> concn. on the degree of Ca-ion concn. is actually much less than provided for by the formula. This holds for both Ringer soln. and serum. A ten-fold increase in HCO<sub>3</sub><sup>-</sup> concn. in a bicarbonate-poor Ringer soln. only decreases the Ca-ion concn. by 20 or 30%. F. S. HAMMETT

**The carbamino reaction of the blood proteins and their alleged importance in the transport of carbon dioxide by the blood.** CAMILLO AUSENDA. *Biochem. Z.* 132, 188-96(1922).—From expts. on blood, serum, ascites fluid, and pleural exudate, no evidence is found that Siegfried's alleged "carbamino-acids" play any part in the transport of CO<sub>2</sub>. If these fluids be satd. with CO<sub>2</sub> in the presence of milk of lime, or Na carbonate or hydroxide and the proteins then pptd. by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or obtained free from simple constituents by dialysis, there is no greater quantity of CO<sub>2</sub> fixed by the protein than in the normal physiol. state of the blood. J. C. S.

**Further experiments on the destruction of lactic acid by yeast.** OTTO FÜRTH AND FRITZ LIEBEN. *Biochem. Z.* 132, 165-79(1922); cf. C. A. 16, 1979.—The disappearance of lactic acid observed on shaking yeast suspensions in a current of O could not be attributed to the formation of simple derivs. such as AcH or  $\beta$ -hydroxybutyric acid, etc.; half of the C of the lost lactic acid does, however, appear as CO<sub>2</sub>, the other half possibly being utilized in the building up of tissue. J. C. S.

**Spontaneous reducing effect of muscle on methylene blue. Physiology of dehydrogenases.** GUNNAR AHLGREN. *Skand. Arch. Physiol.* 41, 1-30(1921); cf. Widmark, C. A. 16, 1962.—By the agency of dehydrogenases occurring in muscle, H is abstracted from certain substances, called H "donators," and added to methylene blue, which is changed thereby to the leuco base. Methylene blue, acting as H acceptor, thus plays the same physiol. role as O. Substances which can act as H donators have sp. dehy-

drogenases. The reducing power of muscle is estd. by detg. the time required for decolorization of known amts. of methylene blue. The red muscle of rabbits and doves has greater reducing power than white muscle. Heart muscle has greater reducing power than skeletal muscle. Seasonal variation in reducing power of frog muscle was observed with a summer max. and a winter minimum. Reducing power is greatest in mammalian muscle. The lowest reducing power is shown by the muscle of worms.

J. C. S.

**Partition of urea in blood.** G. ETIENNE AND M. VÉRAIN. *Compt. rend. soc. biol.* 86, 394-5(1922).—Marked differences are found in the urea contents of blood and blood clot. The amt. of urea found in each component depends on the length of contact between clot and plasma. In expts. with liquids contg. blood corpuscles, addn. of trichloroacetic acid prevents diffusion of urea.

J. C. S.

**Chemical composition of amniotic fluid.** A. LABAT AND M. FAVREAU. *J. méd. Bordeaux* 92, 341-2(1921); cf. Uyeno, *C. A.* 13, 863.—The authors give the following data for the compn. of amniotic fluid: dry matter 13.30, org. matter 6.56, ash 6.81, NaCl 5.25, protein 2.40, urea 0.28%. Dextrose was found occasionally in small quantities. An increase in dry matter, salts, and protein is found during pregnancy.

J. C. S.

**The influence of eating on the bilirubin content of the blood.** E. C. MEYER AND HERBERT KNÜPFER. *Deut. Arch. klin. Med.* 138, 321-9(1922).—In normal people there is a decrease in the bilirubin content of the blood 2-5 hrs. after eating. It begins to rise after 8 hrs. When during the day food is given after a fast since the evening before there is an increase in the blood bilirubin. BaSO<sub>4</sub> causes the bilirubin in the blood to be lessened and 1 l. of H<sub>2</sub>O has no effect. These effects are explained by the fact that foods cause an increase in the secretion of bile into the intestines and either bilirubin is removed from the blood or less of the secreted bile goes into the blood stream. In fasting the bile capillaries are distended with bile, some of which passes into the blood upon feeding. While the greater part of people with liver injury (urobiliruria) show a normal relation, some of them show an increase in bilirubin content of the blood after feeding. This is explained in that the bilirubin reabsorbed from the intestines passes through the injured liver as does urobilin.

J. H. LEWIS

**The lipoids of maternal and fetal blood at the conclusion of labor.** J. M. SLEMON AND H. J. STANDER. *Bull. Johns Hopkins Hosp.* 34, 7-10(1923).—"During the latter part of pregnancy, the fat, lecithin and cholesterol of the blood are more abundant than usual. This change most likely represents a preliminary step in the prepn. for lactation. The mother's blood contains much more of these substances than the fetal blood does. The difference which exists between the 2 organisms in this respect varies from case to case; and the values prevailing in one seem to be entirely independent of those in the other. The placenta is impenetrable to fat and lipoids. Fetal fat, then, must be synthesized, probably from glucose, which is freely supplied by the mother in accord with the demands of her offspring. No characteristic change in the blood fat or lipoids accompanies the development of eclampsia and allied intoxications of pregnancy."

A. P. LOTHROP

**A study of the equilibrium between the so-called "antitrypsin" of the blood and trypsin.** R. G. HUSSEY AND J. H. NORTHROP. *J. Gen. Physiol.* 5, 335-51(1923).—A quant. method of studying the retarding effect of blood plasma on the action of trypsin is given. The following conclusions are reached: The equil. between the inhibitive agent in blood plasma and trypsin is attained almost instantaneously and is rapidly and completely reversible. Expts. in which were studied (1) the effect of adding increasing amts. of plasma to a const. amt. of trypsin, (2) the effect of varying amts. of trypsin with the plasma const. and (3) of diln. of the trypsin-plasma mixt. show a quant. agree-



ment with the law of mass action. Assuming that 1 mol. of trypsin combined with 1 mol. of inhibitor to form 1 mol. of trypsin-inhibitor compd., an equation was found which fits satisfactorily the curves derived from the exptl. data. The reaction in equil. is expressed by the equation:  $\text{trypsin} + \text{inhibitor} \rightleftharpoons \text{trypsin-inhibitor}$ . CHAS. H. RICHARDSON

**Identity of composition of organisms of the same species at the time of death by starvation.** É. F. TERROINE, E. BRECKMANN AND A. FEUERBACH. *Compt. rend.* **175**, 1112-4(1922).—Previous work has proved that the fat content of an organism at the time of death by starvation is identical for all individuals of the same species. The present paper reports detns. of the water, protein and ash in mice and widow-birds (*Vidua principalis*). With normal mice the water content ranged from 60.8 to 74.7, protein 16.25 to 25.0, ash 2.0 to 3.1, fats 2.96 to 8.75. With starved mice the corresponding figures were 75.1 to 77.3, 17.25 to 20.3, 2.5 to 3.3, and 2.3 to 2.47. In normal birds the water was 58.8 to 67.1, proteins 21.62 to 23.87, ash 3.33 to 3.78, fats 4.2 to 11.2. With starved birds the corresponding figures were: 67.8 to 70.4, 22.9 to 26.25, 4.3 to 4.59, and 2.4 to 2.52.

L. W. RIGGS

**Tin in the human organism.** ÉMILE MISK. *Compt. rend.* **176**, 138-41(1923).—Two analytical methods gave identical results. The first was that of Kohn-Abrest (cf. *C. A.* **15**, 812). The second, the Bourcet-Misk method, was as follows: To 100 g. of ground material was added 50 cc. of a 30% soln. of KOH and the mixt. was dried in the oven. The mass was then ground and the powder incinerated in a muffle, the ash being heated to fusion. The fused mass was extd. with boiling water and then filtered. The filtrate was evapd. to dryness, the residue thus obtained was treated with  $\text{HNO}_3$  and evapd. to dryness. This latter residue was taken up with hot water acidified with  $\text{HNO}_3$ . Sn remains as insol.  $\text{SnO}_2$ ; it is collected, washed and weighed. In a man of 42 years the Sn in g. per kg. of dry tissue ranged from 0.0199 in the brain to 0.6316 in lung tissue. The liver and alimentary canal with its contents carried 0.4678 and 0.3077, resp. The liver in 2 fetuses contained 0.599 and 0.3346 g., resp. Sn, therefore, appears to be a normal constituent of human viscera, for which allowance must be made in toxicological analysis. Physiologically the human body appears to contain quite as much Sn as Zn.

L. W. RIGGS

**Fatigue effects as measured by sugar content of the blood.** B. J. JOHNSON. *J. Comp. Psychology* **2**, 155-71(1922).—Sugar content of the blood of 7 children after tests involving fairly complex mental reactions was sometimes increased, sometimes decreased. The exptl. data are meager. The expts. are suggestive but not conclusive.

GEORGE ERIC SIMPSON

**Further investigation of the gonads of *Rhizostoma cuvieri*.** FELIX HAUROWITZ. *Z. physiol. Chem.* **122**, 145-59(1922).—The ash contained K, Na, Ca, Fe, Cl,  $\text{SO}_4$ ,  $\text{PO}_4$ . Fatty acids recognized were formic, caprylic, myristic, palmitic, linolic and linolenic. Glycerophosphoric acid, glycerol, cetyl alc., and cholesterol were also present. S-contg. compds. identified were taurine, *p*- and *o*-cresosulfuric acids and a cystine-contg. protein. Nitrogenous compds. found were trimethylamine, betaine, choline, a peptide contg. leucine and tyrosine, another or several contg. alanine, leucine, tyrosine, glutamic acid and arginine, and one or more proteins which contained in addn. to the amino acids mentioned phenylalanine, cystine, lysine and proline. The presence of a labile lecithin-like substance was indicated as well as a highly unsatd. fatty acid and traces of monomethylamine. The following compds. were absent: stearic, oleic and oxyfatty acids, carbohydrates, glucoproteins, indole derivs., tryptophan, histidine, glycine, hippuric acid, uric acid, purine bases, creatine, creatinine, HCNS, organically bound halogens, and nucleoproteins.

R. L. STEBLE

## G—PATHOLOGY

H. GIDEON WELLS

**Some physical properties of the blood serum in health and disease.** J. KOOPMAN. *Nederland. Tijdschr. Geneeskunde* 67, I, 264-76(1923).—The coagulating temp. of the blood serum is 74-76°, being almost const. in most cases. In some diseases of the kidney and of the blood it is increased considerably. R. BEUTNER

**Investigations about plants which cause hay fever.** C. E. BENJAMINS, J. IDZERDA AND H. UITTREN. *Nederland. Tijdschr. Geneeskunde* 67, I, 330-41(1923).—The frequency and the toxicity of the pollen of certain plants are the factors which det. the cause of hay fever (toxicity means in this case production of allergic symptoms detd. by the skin reaction). Of the 40 plants investigated in Holland, *Festuca rubra* is found to be the most frequent and the most toxic plant. R. BEUTNER

**Wildbolz auto-urine reaction.** HANS STUBBE. *Beitr. klin. Tuberkulose* 50, 262-70(1922).—The results on 85 cases of tuberculosis and 10 normal people are given. The exact details outlined by Wildbolz were followed. The injections were found immediately painful. The autogenous urine test mostly resembled the reaction to 1:10,000 tuberculin, or lay between the reaction to 1:10,000 and 1:1,000, but never equaled the 1:1,000 reaction. It is concluded that inactive tuberculosis specific antigens are liberated and a positive reaction, therefore, indicates an active process. The main drawbacks to the test are the time-consuming element and the technical difficulties encountered in carrying it out. H. J. CORPER

**Serological studies with antigens and antibodies on the surviving artificially perfused spleen.** M. HAHN AND E. V. SKRAMLIK. *Biochem. Z.* 131, 315-19(1922); cf. C. A. 16, 2908.—When homologous erythrocytes are perfused through sheep spleen no changes occur. When heterologous corpuscles (rabbit) are perfused, agglutination and even soln. occur. The effect is attributed to a normal amboceptor in the splenic tissue. When tetanus toxin is perfused its lytic component is largely removed in a few min. It is not possible to recover the toxin. If a spleen treated with tetanus toxin is perfused with rabbit corpuscles a marked agglutination occurs rapidly. *B. coli* are also held up by agglutination in the tissue. The spleen and liver function show a certain agreement in their serological relationships. F. S. HAMMETT

**Lyophobic and lyophobic proteins as antigens and antibodies.** W. G. RUPPEL, O. ORNSTEIN, J. CARL, G. LASCH. *Z. Hyg. Infektionskrankh.* 97, 188(1922). W. G. RUPPEL. *Deut. med. Wochschr.* 49, 40-3(1922).—The amphoteric character of the proteins enables them to form complex mols. with one another. The water-insol. euglobulin is sol. in an aq. soln. of pseudoglobulin. The euglobulin can be sepd. from the pseudoglobulin by the addition of acid, or better, by the action of the elec. current. This tendency toward compd. formation between the protein mols. renders a sepn. almost impossible by ordinary chem. means. This problem is the more difficult because of the tendency of one kind of protein to pass over into another. Albumin is converted partially into pseudoglobulin and euglobulin on long standing in an aq. soln. contg. NaCl. This conversion can be accelerated by alkalizing the albumin soln. and incubating at 37°, or by the action of an elec. current on an aq. soln. of albumin contg. NaCl or  $(\text{NH}_4)_2\text{SO}_4$ . This conversion also occurs in the animal body when the subject is treated systematically with bacterial toxins or other bacterial products. At a certain stage of this systematic immunization the conversion may be so complete that the serum contains nothing but euglobulin. Continued immunization leads to a reestablishment of the normal ratio between the lyophilic and the lyophobic proteins. The serum proteins can best be fractionated as follows: The serum is freed from electrolytes by electrolysis in a 3-cell diffusion app. This leads to a quant. pptn. of the euglobulin, which is removed by

filtration or centrifugalization. The filtrate contg. albumin and pseudoglobulin is now introduced into one of the intermediate compartments of a 4-cell diffusion app.; the remaining compartments are filled with water. The electrodes are contained in the outermost compartments. Passage of the current causes the albumin to diffuse toward the anode and into the protein-free center compartment. This electrolytic method yields pure proteins free from proteoses, peptones, amino acids and lipoids. These electrically prepd. pure proteins were tested for antigenic properties. An albumin-sensitized guinea pig will, as a rule, show no anaphylactic reaction upon reinjection with albumin, but suffers from shock when injected with either euglobulin or pseudoglobulin. Preliminary injection with either euglobulin or pseudoglobulin sensitizes the pigs to both of these proteins, but not to albumin. Euglobulin is by far the best antigen. The reaction to euglobulin and pseudoglobulin, obtained after the preliminary injection of albumin, indicates a partial conversion of the albumin into the other proteins in the body of the pig. The sera of albumin-treated guinea pigs show no precipitin reaction toward any of the proteins. A pseudoglobulin serum is pptd. only by pseudoglobulin. A euglobulin serum is pptd. voluminously by euglobulin and to a small extent by pseudoglobulin, not by albumin. In a specific immune serum the albumins are always free from antibody. Agglutinins and complement-fixation antibodies are chiefly in the euglobulin fraction although a little activity is exhibited by the pseudoglobulin fraction. Bacteriotropins are found in the pseudoglobulin fraction. Since the protective and curative action of an anti-infectious serum is almost exclusively limited to the pseudoglobulin fraction it is concluded that the agglutinins and complement-fixing antibodies, which are in the euglobulin fraction, cannot be responsible for the protective and curative action. The bacteriotropin content of the pseudoglobulin does not account for all the effect of this fraction since sera which have become weak in protective activity by long preservation maintain a full bacteriotropic index. As the hemolytic amboceptor is in the pseudoglobulin fraction it must be distinct from the complement-fixing antibody. The albumin fraction is free from antitoxin, 12 to 15% of the antitoxin is attached to the euglobulin, but the largest percentage appears in the pseudoglobulin fraction. The use of an electrolytically prepd. pseudoglobulin as a vehicle for diphtheria and other antitoxins is suggested.

MILTON HANKE

**The kidney in old age.** WILHELM NYERI. *Wiener Arch. inn. Med.* 5, 147-194 (1922).—Urine exams. of 56 patients over 60 years of age indicated normal kidney function in 33%. The concn. power of the kidney was reduced in 20%. Iodine elimination was not delayed. By the methods of Ambard, the chloride balance was normal in all cases, while 10% showed urea retention. Residual N was increased in only a few cases; of this residual N 50-60% was urea. In all but 11 cases normal values were found for the albumin of the blood. The urinary findings did not vary greatly from the normal. Slight albuminuria and the presence of erythrocytes and casts was noted, and polyuria and hypostenuria were relatively common. Histological study of the kidneys in a number of cases showed a more or less marked atherosclerosis of the medium and large blood vessels, with a beginning angiosclerosis in some cases at times associated with slight degenerative changes in the parenchyma of the kidney. H. F. H.

**Comparative concentration of urea in the blood and saliva in a series of pathologic cases.** H. W. SCHMITZ. *J. Lab. Clin. Med.* 8, 78-82 (1922).—Comparative simultaneous analyses on 45 specimens of blood and saliva, representing various pathologic conditions, are reported. The urea content of saliva averaged 89.4% of that of the blood. Salivary urea detn. may be employed in detg. the functional activity of the kidneys where for any reason it is impracticable to obtain blood specimens. E. R. LONG

**The secretion of gastric juice in health and disease.** A. J. CARLSON. *Physiol. Rev.* 3, 1-40 (1923).—A review with full bibliography, including a discussion of the

methods of obtaining gastric juice, the factors inducing gastric secretion, the composition of the juice, and the secretion in disease. Essential hypersecretion probably does not exist; the factors definitely known to induce hypersecretion are disturbances in motility. E. R. LONG

**Cellular immunity: congenital and acquired tolerance to non-protein substances.** J. A. GUNN. *Physiol. Rev.* 3, 41-74(1923).—A review with bibliography on natural and acquired tolerance to strophanthus and toad poison, cantharidin, atropine, alcohol, ether, artificial hypnotics, *Cannabis indica*, opium alkaloids, cocaine, caffeine, nicotine and arsenic. Caution is urged in accepting results which have been claimed to show an augmentation of destruction of alkaloids given in small amts. and for short periods, and especially those results where a new power of destruction seems to be originated by habituation. E. R. LONG

**Destruction of red blood corpuscles in health and disease.** PEYTON ROUS. *Physiol. Rev.* 3, 75-105(1923).—A review with extensive bibliography. E. R. LONG

**The etiology of rickets.** E. A. PARK. *Physiol. Rev.* 3, 106-163(1923).—A critical review with extensive bibliography, with a discussion of the results of clinical observation and expt. Two factors exist, the one in radiant energy, the other in an unknown form in certain foods, especially cod-liver oil, which are capable of preventing rickets from developing, or continuing if it is established. Although the ultimate nature of the effect of these factors is obscure, it is known that they regulate metabolism in some way, particularly with respect to Ca and P. E. R. LONG

**The bile factor in pancreatitis.** F. C. MANN AND A. S. GIORDANA. *Arch. Surg.* 6, 1-30(1923).—A reflux of bile could not have been the cause in any of the cases of acute pancreatitis studied. JOHN T. MYERS

**Experiments in traumatic shock.** MCKEEN CATTELL. *Arch. Surg.* 6, 41-84(1923).—In the normal subject the inhalation of strong ether results in a sudden drop in the arterial pressure which is quite temporary. In the shocked animal there is no recovery of the blood pressure and the pressure continues to fall to zero.  $\text{N}_2\text{O}$  and O in favorable proportions will cause only a slight drop in pressure. Large intravenous doses of adrenaline but not of pituitary extract will remove the sensitiveness to ether for about an hour. JOHN T. MYERS

**A comparison of the colloid flocculation test (Dreyer-Ward technic) with the Wassermann reaction for the diagnosis of syphilitic infection.** H. J. B. FRV. *J. State Med.* 30, 396-407(1922).—The flocculation test is modified by increasing the period of incubation to 24 hrs., especial care being taken to maintain sterility. Of 1001 specimens, discrepancies were found in 4%; 3.6% in the case of sera, 4.8% with cerebrospinal fluids. Treatment modifies the flocculation test more rapidly than the Wassermann reaction. GEORGE ERIC SIMPSON

## H—PHARMACOLOGY

ALFRED N. RICHARDS

**The action of hypophysis extracts on the respiratory center.** U. G. BIJLSMA. *Nederland. Tijdschr. Geneeskunde* 66, I, 2461(1922).—Small quantities of hypophysis ext., injected intravenously into a decerebrated cat, cause a temporary irritation, large quantities, viz.: more than about 0.5 cc., block the respiratory center. R. BEUTNER

**The influence of organic antimony compounds on trypanosomes in animals.** M. D. HORST. *Tijdschr. vergel. Geneeskunde* 6, 89-94(1921).—H. has stated previously (*C. A.* 14, 2033) that suspensions of  $\text{Sb}_2\text{O}_3$ , injected into rabbits, kill trypanosomes. Various insol. Sb compds. are now tested. "p-Urethanophenylstibium sulfide" kills trypanosomes *in vitro* instantly, *in vivo* more slowly; it is less active than tartar emetic.

"*p*-Urethanophenylstibic acid" and its sodium salt have some action. "Antimonyl-stibinacetine" has no action.

R. BRÜTNER

**Miscellaneous tests of carbon tetrachloride as an anthelmintic.** M. C. HALL AND J. E. SHILLINGER. *J. Agr. Research* 23, 163-92(1923).—Tests of  $\text{CCl}_4$  on various animals and on man are described.  $\text{CCl}_4$  is an effective drug for removing blood-sucking strongyles. It has a rather high efficacy against ascarids in certain species of host animals. Based on wt. of animal the tolerance of  $\text{CCl}_4$  for different species of animals is given.

F. C. COOK

**Lime therapy of pulmonary tuberculosis.** RUDOLF LEUCHTENBERGER. *Beitr. klin. Tuberkulose* 50, 322-44(1922).—In the early stages of the disease lime administration, especially in its most active form by inhalation, can have a preventive or healing influence. These results are brought about by changes in the nature of the entire organism, a change in constitution. In later stages of the disease the lime acts purely symptomatically, without in the slightest acting upon the basic disease.

H. J. C.

**Some cases of poisoning by methanol.** E. LAMBLING AND C. VALLÉE. *Arch. intern. physiol.* 18, 617-9(1921); *Physiol. Abstracts* 7, 59.— $\text{MeOH}$  is fatal in doses of 30 grains and toxic in those of 8 grains. Symptoms: violent headache, pain in the digestive tube with subsequent blindness.

H. G.

**Morphine tolerance.** V. J. BIBERFELD. *Biochem. Z.* 122, 260-8(1921); *Physiol. Abstracts* 6, 588; cf. *C. A.* 11, 667.—Attempts were made to break the tolerance of dogs to successive doses of morphine. Withdrawals of blood or subcutaneous administration of protein (milk) effected a temporary break. Injections of acid or alkali were without effect.

H. G.

**Parasympathetic poisons and blood sugar.** A. BORNSTEIN AND R. VOGEL. *Biochem. Z.* 122, 274-84(1921); *Physiol. Abstracts* 6, 580; cf. *C. A.* 15, 2926.—Excitants of the parasympathetic nervous system, such as pilocarpine, physostigmine, choline, and acetyl choline, increase the blood-sugar content of normal dogs. Atropine inhibits (to a greater or lesser extent) this glucemia. In some diabetic patients intravenous administration of atropine depresses the sugar content of the blood.

H. G.

**Action of pituitrin on saline diuresis.** F. PENTIMALLI. *Sperimentale* 75, 145-59(1921); *Physiol. Abstracts* 6, 383.—Experimenting with dogs, P finds that if diuresis is produced by intravenous transfusion of saline, it is only slightly affected by the injection of pituitrin. This substance produces an immediate stoppage of the flow of urine, this being due to a renal vasoconstriction; the stoppage, however, is of very short duration; the diuresis reappears, and continues as if no pituitrin had been injected. Pituitrin further causes a very transient fall of blood pressure under these conditions; to this fact, as well as to the vasoconstriction produced, is due the slight antidiuretic action of the substance.

H. G.

**Prevention of goiter.** DAVID MARINE. *Public Health* (Mich. St. Bd. Health) 11, 23-4(1923).—Simple goiter is the easiest known disease to prevent. 100-200 mg. of I taken twice a year is sufficient to prevent the disease. Max. storage capacity of thyroid gland not over 30 mg. I.

JACK J. HINMAN, JR.

**A new collective poisoning by arsenic.** M. F. CARRIEU AND M. FABRE. *Rev. hyg.* 14, 993-9(1922).—Poisoning of about 100 persons (4 deaths) due to the accidental addn. to wine of an As compd. Content of wine 0.018 to 0.040 g. As per l. Distribution suggested epidemic disease. Bibliography.

JACK J. HINMAN, JR.

**Chloroform in the blood after death.** C. S. GIBSON AND P. P. LAIDLAW. *Guy's Hospital Reports* 1922, 359-66.—Extns. of the  $\text{CHCl}_3$  in the heart blood of rabbits killed by an overdose of  $\text{CHCl}_3$  show a larger amt. a few days after death than at death, an increase apparently due principally to the passage of liquid from the vascular system after death.

J. C. S.

**Effects of extracts of *Ascaris vitulorum* on experimental animals.** B. SCHWARTZ. *Philippine J. Sci.* 22, 109-14 (1923).—Saline exts. of *Ascaris vitulorum* were toxic to guinea pigs and rats and nontoxic to frogs and a turtle. In susceptible animals toxic symptoms were produced by intraperitoneal injection and in one case by feeding. In one expt. toxicity was not destroyed by boiling. The symptoms closely resembled those produced in calves parasitized by the organism. These data afford striking evidence in favor of a chem. pathology in a sp. parasitic disease. H. B. LEWIS

**Preliminary note on the therapeutic action of Bayer 205 in nine cases of human trypanosomiasis.** G. C. LOW AND PHILIP MANSON-BAHR. *Lancet* 1922, II, 1265-7.—Of 8 cases of *T. gambiense* infection in man treated with Bayer 205 (compn. not published by manufacturers) 7 were apparently cured, while one died with cerebral trypanosomiasis. One case of *T. rhodesiense* infection was improved but not definitely cured. E. R. LONG

**Quinidine in auricular disease.** JOHN PARKINSON AND J. W. MCK. NICHOLL. *Lancet* 1922, II, 1267-70.—From results with 35 cases the conclusions are: In paroxysmal auricular fibrillation quinidine is indicated, for in some cases it either inhibits the attacks or reduces their incidence. No other drug, not even digitalis, will do this. In paroxysmal tachycardia it has little or no effect. In auricular flutter it is sometimes effective alone or after digitalis. In a small proportion of cases with established auricular fibrillation quinidine restores normal rhythm which continues indefinitely, but in most cases it is not effective, or if so only temporarily. E. R. LONG

**The effect of intravenous sodium bicarbonate on intestinal movements.** C. E. KING AND J. G. CHURCH. *Am. J. Physiol.* 62, 459-72 (1922).— $\text{NaHCO}_3$  injected intravenously into dogs (50 cc. of 2.5%, 4% and 6% soln.) usually produces an increase in tonus of the intestine, often local rhythmical and occasionally peristaltic movements. It is not clear what part of the  $\text{NaHCO}_3$  is responsible for the action. There is a parallelism between the intensity of action and amt. of  $\text{NaHCO}_3$  given. Acid diminishes or abolishes the action; but the results with  $\text{NaHCO}_3$  solns. of varying  $p_H$  were not definite enough to warrant the conclusion that the action is due to alkalinity. Neither  $\text{CO}_2$ , nor a disturbed Na:Ca ratio appear to be responsible for the action. The point of attack is peripheral in the enteric nervous mechanism. J. F. LYMAN

**The action of adrenaline on the human stomach.** Administered intravenously or by mouth. D. DANIELOPOLU AND A. CARNIOL. *Compt. rend. soc. biol.* 87, 716-8 (1922).—The gastric contractions were recorded by means of a rubber balloon in the stomach connected to a Marey tambour. An intravenous injection of very small doses of adrenaline (1 cc. of a 1:500,000) produces an increased gastric contraction in man. Much stronger doses (1:100,000) or even more concd. solns. give a temporary inhibition of the gastric contractions followed by increased contractions. Given by mouth 1 mg. of adrenaline generally occasions a strong excitation of the gastric contractions. Since a large portion of the adrenaline is destroyed by the gastric juice it is thought that the stimulating effect is due to vagotropic action of the remaining traces. Conclusion: The use of adrenaline as a hemostatic in gastric ulcers is absolutely contraindicated. **The action of atropine on the human stomach.** *Ibid* 719-20.—Very small doses of atropine given intravenously ( $\frac{1}{30}$ - $\frac{1}{4}$  mg. of the sulfate) definitely increase the gastric contractions, but much stronger doses cause complete inhibition. **Action of calcium on the human stomach.** *Ibid* 721-2.—Intravenous injections of  $\text{CaCl}_2$  (100 mg.) cause an increase in gastric contraction; larger doses (250 mg. and more) bring about inhibition. Introduced directly into the stomach small doses (200 mg.) increase the contractions but doses of 0.5 to 1.0 g. or more cause definite inhibition which may be of long duration. **The action of eserine on the motility of the human stomach.** *Ibid* 722-4.—Eserine is recognized as purely vagotropic substance. The authors, however, contend

that it excites both the vagus and the sympathetic. **The physical element in gastric motility of man.** *Ibid* 724-7.—Under the psychical stimulation of an appetizing meal eaten by another gastric contractions began after a brief interval, gradually grew stronger and continued after the stimulation had ceased. In another expt. atropine was injected intravenously enough to suspend the gastric motility; under the same psychic influence as before the stomach contracted with great energy, but the contractions were again suspended by a second atropine injection. Similar results were obtained with eserine, except that the psychic contractions of the stomach already under the influence of eserine commence much quicker than with the normal stomach. S. MORGULIS

**The chemistry and pharmacologic action of thyroxin.** E. C. KENDALL. *Ann. Clin. Med.* 1, 256-8(1923).—Thyroxin acts as a catalyst. The mol. is about 65% I. I without the nucleus is physiol. inactive. The effect of the nucleus without I is unknown. JOHN T. MYERS

**Further observations on the influence of salts when injected into the animal body.** R. G. HUSSEY. *J. Gen. Physiol.* 5, 359-64(1923).—When 2.4 M NaCl and equimol. solns. of NaHCO<sub>3</sub>, KH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, LiNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub> are injected into rabbits there is a decrease of approx. 70% in the circulating mononuclear cells of the blood. At 1/2 to 1/4 this concn., the decrease of blood cells is about 1/2 as great. The injection of solns. of sucrose and glycerol, equiosmotic with 2.4 M NaCl, caused no significant decrease in the blood cells. The max. decrease is reached 3 hrs. after an injection; the blood picture is normal again in 24 hrs. The cations are probably responsible for the results obtained. The analogy with the effects of X-radiations (C. A. 16, 2542) is commented on. It is suggested that the biol. effects here are due to chem. reactions produced by the X-radiations. CHAS. H. RICHARDSON

**Arsenobenzene in the treatment of syphilis.** C. H. MILLS. *J. State Med.* 30, 507-39(1922).—A comprehensive discussion of clinical findings. G. E. S.

**Bismuth compound of the aromatic series in the therapy of syphilis.** H. GRENET, H. DROUIN and L. RICHON. *Bull. acad. med.* 87, 658-61(1922).—The "Na deriv. of trioxybismutho-benzoic acid (C<sub>12</sub>H<sub>7</sub>O<sub>3</sub>Na<sub>3</sub>[COOBi(OH)<sub>2</sub>]<sub>3</sub>)" appears to be as efficacious as the As compds. in the therapy of syphilis, having the same effects upon the clinical and immunological pictures. G. H. SMITH

## I-ZOOLOGY

R. A. GORTNER

**The fats and lipoids of the ovarian egg of the carp (Cyprinus carpio).** F. FAURÉ-FREMIET and HENRIETTE GARRAULT. *Bull. soc. chim. biol.* 4, 428-34(1922); cf. C. A. 16, 3133. A. T. CAMERON

**Investigations on (1) the effect of a direct electric current, (2) of some chemicals, on the ciliary motion of the anadonta gill.** ELSA SEGERDAHL. *Skand. Arch. Physiol.* 42, 62-76, 77-80(1922); *Physiol. Abstracts* 7, 12.—(1) Closure of direct current has no effect or a weak stimulant action on the cilia of the Eckzellen (? fronto-lateral cilia). On the cilia of the "Seitzellen" (? frontal cilia) it causes inhibition when the current passes from base to ciliated surface of a cell, weak stimulation in the other direction. (2) Of the substances tested (glucose, NaCl, chloral hydrate, amylene hydrate, cocaine), all depress ciliary action. Distd. water, however, primarily accelerates it. H. G.

**The extract of Melolontha vulgaris.** II. D. ACKERMANN. *Biol.* 73 (N. F. 55), 319-21(1921); *Physiol. Abstracts* 6, 479; cf. C. A. 14, 3281.—The arthropod metabolism (like that of the Crustacea) leads to a piling up of arginine, but creatinine and Me guanidine are absent. H. G.

**The excretion of a detoxicating substance by ciliates.** V. GRUBER. *Centr. Baktr. Parasitenk., I Abt.* 89, 87-90(1922).—A large no. of ciliates (paramecia and

colpidia) will live longer in a toxic substance than a small no. This is explained by the fact that a large amt. of a detoxicating substance, called tectin, is produced in the capsule. In methylene blue the excreted tectin is stained blue and may be seen. J. H. L.

**A new culture method for protozoa.** AMSTER. *Centr. Bakt. Parasitenk.*, 1 Abt. 89, 166-8(1922).—A culture of ciliates free from bacteria was obtained by growing in a 1:1000 soln. of peptone in distd.  $H_2O$  contg. enough  $HCl$  to produce an acidity of  $pH$  6.8. The cultures are kept at 22-5°. These conditions favor the growth of the protozoa and are unfavorable for bacteria. The abs. sepn. is accomplished by electrolysis, the protozoa going to the cathode and the bacteria to the anode. JULIAN H. LEWIS

**The attraction of common flies by the substances of fermentation and putrefaction.** E. ROUBAUD AND R. VEILLON. *Ann. inst. Pasteur* 36, 752-64(1922).—Count and species identification was carried out on flies attracted by various chemicals and trapped in a special app. Sugars and saccharine non-fermented products, alcs., and  $NH_3$ , in general exerted only slight chemotropic action.  $NH_4HS$ ,  $NH_4$  valerianate, valeric acid and  $NMe_3$  were especially active. Yeast ext. was only feebly active. Maceration of meat was markedly attractive, putrefying meat of less activity, sea fish feebly active, while macerations of pears and potatoes were strongly attractive. The meat fly (*C. erythrocephala*) was particularly attracted by vegetable substances. The max. attraction for the egg-laying female of the house fly was fermenting horse manure. E. R. LONG

**The occurrence of copper and zinc in certain marine animals.** HAZEL W. SEVERY. *J. Biol. Chem.* 55, 79-92(1923).—The Cu and Zn contents of the following marine animals of the Pacific coast were investigated: sea anemone, black, yellow and red starfish, sea urchin, yellow slug, Cal. oyster, clams, mussels, abalone, cryptochiton, shrimp, crab, salmon, sea-lion and whale. Cu was present in all except the clam and whale, the av. amt. being 0.497 mg. per kg. Zn was present in all the animals, the av. amt. being 4.25 mg. per kg. The distribution of Cu and Zn in the cryptochiton was not uniform, the blood contg. the greatest amt. of Cu and the least amt. of Zn. The Cu which is in combination with protein unites with  $O_2$  to form oxyhemocyanin. The mantle carried the largest amt. of Zn but an amt. of Cu lower than that in the blood. The Zn content of the Cal. oyster was the highest of all the samples analyzed but was much lower than that of the eastern oyster. The sea-lion and whale, being mammals, do not carry Cu to any extent and the Cu in the sea-food eaten does not seem to be accumulative. Zn, however, was present in the muscle, spleen, liver, blood and bile but in amts. less than that found in the oyster. Cu is present in the lower forms of sea animals as an O carrier in place of the Fe of mammals but environment does not seem to change the sea-lion and whale in this respect. The function of the Zn is not clearly known but it may be present as an aid to enzymic action in a manner not understood. A. P. LOTHROP

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

**Report of committee to coöperate with other committees on food definitions.** WM. FREAR, et al. *J. Assoc. Official Agr. Chem.* 6, 169-71(1922).—Definitions and standards for canned corn, tomatoes, strained tomatoes and tomato paste are reported as adopted. H. A. LEPPER

**Report on canned foods.** R. W. BALCOM. *J. Assoc. Official Agr. Chem.* 6, 49-51 (1922).—Changes as given are recommended for official adoption in the wording of the Howard methods for the microanalysis of tomato pulp, catsup, purée, sauce and paste to secure greater accuracy and clearness. H. A. LEPPER

**Report on arsenic in foods.** R. M. HANN. *J. Assoc. Official Agr. Chem.* 6, 31-4



(1922).—Collaborative results on the Gutzeit test and Farr modification are reported with the recommendation for further study of both.

H. A. LEPFER

**Report on preservatives (saccharin).** M. G. WOLF. *J. Assoc. Official Agr. Chem.* 6, 14-15(1922).—To prep. the sample in the detn. of saccharin in baked-food products treat with a mixt. of  $H_2O$  and alc., heat the hydroalcoholic soln. on the steam bath until most of the alc. is evapd. and a molasses-like residue remains, add an equal vol. of petr. ether and a little coarse sand, stir and evap. the petr. ether and repeat until the mass becomes spongy and jelly-like, and the odor of alc. is faint, spread on a large watch glass and heat in a  $H_2O$  oven until dry, scrape off and powder in a mortar, and ext. with  $Et_2O$ . No analytical results are given.

H. A. LEPFER

**The vitamin and the vitamin bunk.** H. C. LYTHER. *Gen. Sci. Quart.* 7, 112-23 (1923).—Mainly about abuses by com. houses and their relation to food and drug laws and to advertising law.

E. J. C.

**Locusts as a food.** ANON. *J. Dept. Agr. Union S. Africa* 6, 5(1923).—The compn. of the powder resulting from grinding sun-dried, adult, brown locusts (*Pachytelus sulcicollis*) is: moisture 9.05-11.62, ash 5.12-5.56 (contg.  $SiO_2$  1.31-1.75,  $CaO$  0.27 to 0.28,  $K_2O$  0.52,  $P_2O_5$  1.36-1.59%), ether ext. 10.91-11.19, crude fiber 11.26, and protein 56.32-59.60%. Owing to their high protein content, dried locusts, if used for stock or poultry food, should be mixed with other foods high in carbohydrates.

K. D. JACOB

**Determination of amino acid nitrogen in foods by the quantitative colorimetric method.** H. RIFFART. *Z. Nahr. Genussm.* 44, 225-39(1922).—The following solns. are required: (1) A stock soln. contg. 100 mg. of amino acid N per l. A soln. of 0.9506 g. of asparagine per l. may be used. The stock soln. is dild. to make standard comparison solns. contg. 20, 18, 16, 14, 12, 10, 8, 6, 4, and 3 mg. per l. All are preserved with toluene. (2) 9.078 g.  $KH_2PO_4$  per l. (3) 11.876 g.  $Na_2HPO_4 \cdot 2H_2O$  per l. (4) A mixt. of (2) and (3) in the proportion 2:3. (5) 0.1 g. neutral red in 1000 cc. of 50%  $C_2H_5OH$ . (6) 0.1 N, 0.01 N, 0.0025 N  $NaOH$  and  $H_2SO_4$ . (7) 1% ninhydrin in water. The neutral red soln. should be made up frequently and kept in a brown bottle. The ninhydrin should be purchased in 0.1 g. ampules and made up fresh each time. The soln. under examn. should be freed from proteins by dialysis and from  $NH_3$  by vacuum distn. Its amino acid N content should not exceed 20 mg. per l. Two cc. of each of the standard test solns. of the phosphate mixt. and of the unknown are pipetted into sep. dry test-tubes. One drop of neutral red soln. is added to each. The color of the phosphate soln. is exactly matched by suitable addn. of acid or alkali to the other tubes, unnecessary increase in vol. being avoided. To each of the neutralized test solns. are added 2 cc. of the phosphate mixt. and 1 cc. of the ninhydrin soln. The tubes are shaken, placed in a rack and held in a boiling water bath until the 3 mg. per l. standard exhibits a blue-violet color (about  $\frac{1}{2}$  hr.). When observing the color, remove the whole rack, so that the color, which is greatly influenced by heat, will be uniformly developed. The solns. are then cooled to room temp., allowed to stand  $\frac{1}{2}$  hr., made up to 100 cc. and color comparisons made. The relation between decompn. and increase in content of amino acid N was investigated in *beef, horse flesh and veal*. Detns. were also made in raw and boiled *milk* and other foods.

D. B. DILL

**The digestibility of protein after hot or cold pressing.** J. A. EZENDAM. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* 27, 203-13(1922).—The digestibility of the protein of linseed cake and other animal food is detd. by the HCl-pepsin method. No difference is found with cold or with hot pressing of the cake.

R. BRUTNER

**Milk.** P. DE SORNAY. *Rev. agr. Maurice* 1, 275-83(1922).—Analyses of milk samples from Mauritius and other countries are given. The present law in Mauritius should be changed so as to require 12% dry substance with 3-3.5% butter fat. Some

popular misconceptions are corrected, regarding the value of the lactometer for detecting adulteration, and concerning the effect of the water and feed ingested on the compn. of the milk. F. W. ZERBAN

**Bacteria counts of milk products obtained by the microscopic method.** G. C. SUPPLEE AND V. J. ASHBAUGH. *J. Dairy Sci.* 5, 570-82(1922). E. J. C.

**The casein particles suspended in the milk (milk platelets).** E. HEKMA. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* 27, 13-22(1922).—Methods for microscopic observation of milk platelets, which are analogous to those of the blood. In filtering through a Chamberland candle the milk platelets stick to the candle. Freshly formed cheese is a net-work of such platelets which play an important role in the pptn. of the milk. R. BEUTNER

**A wire-shaped substance appearing in milk on precipitation by rennet.** E. HEKMA. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* 27, 75-81(1922).—The ppt. produced by rennet in milk consists of the milk platelets (cf. preceding abstract) and of a coagulate which has the form of a wire. As to the chem. compn. of this last substance no decision can be reached. It may be fibrin or tyrosine, but is certainly not a fatty acid. R. BEUTNER

**Determination of the milk content of milk chocolate.** J. GROSSFELD. *Z. Nahr. Genussm.* 44, 240-4(1922).—The method of Baier and Newmann (*C. A.* 4, 353) is compared with new methods. The first of these is based on the high lime content of milk ash. *Detn. of CaO in ash* is as follows: Completely ash 20 g. of chocolate and treat the ash with exactly 20 cc. of 25%  $H_3PO_4$ ; this dissolves the lime. Add exactly 20 cc. of 2%  $(NH_4)_2C_2O_4$  and, after stirring, exactly 20 cc. of 10% NaOH. The same reagents are used in like quantity to det. the effective strength of the permanganate soln. Both mixts. are allowed to stand until cool, and are then filtered through a kieselguhr filter. 20 cc. of 1-3  $H_2SO_4$  are added to 50 cc. of each filtrate and titration with 0.1 N  $KMnO_4$  follows. If the difference in vols. used is  $d$  then  $CaO = (100 \times 60 \times 0.005607d) / 20 \times 50 \times 2 = 0.0188d\%$ . If the ash content of the chocolate is  $a$  and the CaO content is  $b$  then the % of milk solids =  $5.56b - 0.246a$ . As calcd. from the av. ratios of N to ash in these products the % of milk protein =  $26.1b - 1.16a$ . Also it may be calcd. from the formula, milk protein =  $21.4b - 1.35N$ , where  $N$  = total N of original chocolate. *Detn. of milk protein in 18 chocolates* by the original method of Baier and Neumann and by the formulas shown above gave close agreement. The procedure based on the CaO content and total ash detns. is simplest. D. B. DILL

**Colorimetric investigations on dyes for butter and cheese.** H. A. SIRKS. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* 27, 62-73(1922).—A method for detg. the coloring power of the dyes is given. The dyes are dissolved in  $CHCl_3$ . R. BEUTNER

**The separation of cream according to the Friesish system.** W. VAN DAM AND H. A. SIRKS. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* 26, 106-80(1922).—To study the influence of viscosity on the sepn. of cream from milk various substances which do not influence the sp. gr. of the milk plasma were added. Saleb, tragacanth and other similar substances considerably augment the sepn. This is due to the fact that the fat corpuscles conglomerate more readily and, therefore, move upwards more rapidly. Gum arabic, starch, and gelatin have similar but not so pronounced action. No relation was found between the sepn. of cream and the CaO and  $H_3PO_4$  content of the milk. The varying adsorption of protein to the fat corpuscles is found to have no influence in fresh milk but did affect the sepn. in old milk. The surface tension between milk fat and milk plasma detd. according to the method of Morgan and Stevenson (*Z. physik. Chem.* 63, 151) had no effect on cream sepn. The properties which chiefly influence the sepn. of the cream are characteristic of the milk plasma, not of the fat. Alkali and acid both decrease the velocity of sepn. with fresh milk. With old milk alkali has very little

influence. The sepn. of the cream in a milk in which the fat corpuscles are solid is better the lower the temp. This is due to a more or less rapid crystn. of the fat. The Friesish system takes advantage of this.

R. BRUNNER

The composition and dietetic value of "ambrosia." ANON. *J. State Med.* 30, 540-6(1922).—This dried milk prepn. contains  $H_2O$  2.04, fat 32.37, protein 27.77, lactose 32.67, mineral matter 5.15%. Bacteriol. reports on the original milk and on the "reconstituted" milk are given.

GEORGE ERIC SIMPSON

Testing buttermilk. J. W. MITCHELL. *N. Y. Prod. Rev. and Am. Creamery* 53, 666, 668, 733-8(1922); *Expt. Sta. Record* 46, 680.—Owing to the inaccuracy of the Babcock test the Am. Assoc. of Creamery Butter Manufacturers has worked out a test which seems to check closer with the chem. analysis than the Babcock test. The regular Babcock glassware is used, and for the test 2 cc. of *N* Bu alc. is added to the bottle, followed by 9 cc. of buttermilk, and then from 7 to 9 cc. of conc.  $H_2SO_4$ . It is then centrifuged according to the rules for making the Babcock test. By using this new test for buttermilk at different creameries, the following factors were found to decrease the fat lost in buttermilk: (1) a good quality of cream, (2) a churning temp. sufficiently low that it will take 45 to 50 min. to churn, at the speed to produce the greatest concussion, with the churn  $1/3$  to  $1/2$  full, and (3) holding the cream at least two hours at churning temp. before churning.

H. G.

Pure leaven culture. A. FORNET. *Umschau* 26, 754-6(1922).—A short account of the success obtained in producing a standard leaven to be used in place of yeast in bread making.

E. G. R. ARDAGH

The chemistry of the strength of wheat flour. H. E. WOODMAN. *J. Agr. Sci.* 12, 231-43(1922).—Samples of gliadin and glutenin isolated from typical strong and weak flours investigated by the racemation method gave results which are suggestive in relation to their bearing on the existing ideas of flour strength, since it is shown that gliadins from weak and strong flours are identical proteins but glutenins prep'd. from the same sources are 2 distinct chem. compds. Existing ideas on flour strength are to be modified. The factor which det's. size is most probably connected with the diastatic capacity of the flour, while the factor which det's. shape which appears to be directly related to the phys. properties of the gluten of the flour is dependent on the particular glutenin mechanism possessed by the wheat. It is demonstrated that proteins can be ext'd. by 0.2% KOH without suffering change.

R. B. DREMER

Significance of wheat hairs in microscopical examination of flour. G. L. KEENAN. U. S. Dept. Agr., *Bull.* 1130, 1-7(1923).—Flours made from purified middlings material show a lower hair count than those contg. lower-grade mill stocks, and the possibility is therefore suggested of making a classification of flours based on the hair count alone.

W. H. ROSS

Lactated flours and flours for pap. R. LECOQ. *Bull. soc. hyg. aliment.* 10, 552-80(1922).—L. discusses the use of lactated flours, lactated mixts. (so-called), "comp'd. alimentary flours," malted flours, condensed and conc'd. milks, and pap flours for feeding infants. He gives numerous analyses of French com. prepus. (generally of doubtful value). Lactated flours and "comp'd. alimentary flours" are essentially incomplete foods.

A. P.-C.

Report on meat and meat products. C. R. MOULTON. *J. Assoc. Official Agr. Chem.* 6, 72-6(1922).—Collaborative study of methods for detg. sugar in meats showed further study to be necessary. The recommendation for modification of the method for nitrates and nitrites directing the use of a standard soln. of  $C.P. NaNO_3$  instead of calcg. from the vol. of gas was warranted.

H. A. LEPPER

Determination of crude fiber in prepared mustard. C. A. CLEMENS. *J. Assoc. Official Agr. Chem.* 6, 205-7(1922).—Macerate 10 g. in a beaker with 95% alc. Wash

on to a 12.5-cm. filter with alc. Remove alc. with suction and wash 3 times with  $\text{Et}_2\text{O}$ . Transfer with paper to extractor and ext. with  $\text{Et}_2\text{O}$  for 1 hr. Transfer the main bulk to the digestion flask, remove  $\text{Et}_2\text{O}$  and dry the paper. Transfer the remainder of the sample to the flask with 1.25%  $\text{H}_2\text{SO}_4$ . Det. crude fiber by the official method. Results on 32 samples are lower than those by the unmodified official method. No correlation between the fat content and differences by the 2 methods is evident. Max., min. and av. % of solids, ash, NaCl, acid,  $\text{Et}_2\text{O}$  ext., protein, carbohydrates and crude fiber are given for 32 samples.

H. A. LEPPER

Methods of determining the number of microorganisms in tomato products. C. A. DARLING. N. Y. Agr. Expt. Sta., *Tech. Bull.* 91, 56 pp. (1922). E. J. C.

Canned spinach as a source of botulism. RUTH B. EDMONSTON, CHARLES THOM AND L. T. GILTNER. *Am. Food J.* 18, No. 1, 33-6 (1923).—Results of an investigation on 401 cans of spinach of a particular pack responsible for the outbreak of botulism at Kendallville, Indiana, are given. Methods theoretically and generally practically adequate had been followed in the cannery. Cans found free from spoilage by inspection, appearance of unopened can, vacuum present, and the odor and appearance of the spinach were free from evidence of bacterial activity as detd. by culture. Swells were found to carry active bacterial contamination or to be pronounced examples of chem. corrosion. Exptl. inoculation with resealing and incubation of 64 cans was made. Toxin sufficient to kill guinea pigs was formed in 3 before gas or odor or both developed sufficiently to make possible their removal by inspection. Among large numbers of cans handled under widely diff. storage conditions, the occurrence of an occasional can in which the toxicity has reached the danger point before gas or swell is detectable is clearly a possibility with spinach. Careful inspection before opening and actual re-cooking of the product as it comes from the can should be followed. Incubation under observation at the factory is recommended together with the use of batch nos. or storage of unit lots to insure the detection and sepn. of undercooked lots from any cause. These lots should be reprocessed after removal of swells.

H. A. LEPPER

Composition of Russian cooking salt. E. SARIN. *Z. Nahr. Genussm.* 44, 244-51 (1922).—Description and compn. of 68 samples are given. D. B. DILL

Report on the determination of moisture in dried fruits. R. W. HILTS. *J. Assoc. Official Agr. Chem.* 6, 40-8 (1922).—Various procedures for the detn. of  $\text{H}_2\text{O}$  in dried apricots, peaches, pears and apples were studied. Drying in an atm. of H at  $100^\circ$  causes as much caramelization as drying in air. The official method of drying over  $\text{H}_2\text{SO}_4$  without heat using  $\text{Et}_2\text{O}$  to obtain a high vacuum gave in 2 months only  $\frac{1}{4}$  of the loss observed by heating *in vacuo* at  $70^\circ$ . The distn. method of Dean and Stark (*C. A.* 14, 2145) using xylene, toluene, kerosene, amyl acetate, and combinations gave promising results on apples but not on other fruits. A full discussion of exptl. work precedes the directions of a method for drying 10 g. in an Al dish, 8.5 cm. in diam., placed directly on a metal shelf in a vacuum oven at  $70^\circ$  with a pressure not over 4 in. of Hg for 12 hrs. Admit 2 bubbles of air per sec. through  $\text{H}_2\text{SO}_4$ . Cover the dishes with tops, cool in a  $\text{H}_2\text{SO}_4$  desiccator and weigh as soon as cool. Collaborative results by this method were satisfactory but those in a  $\text{H}_2\text{O}$  oven at  $100^\circ$  were not for pears, peaches and apricots. Apples were not tried by collaborators. Results on 52 samples of apples showed that drying a 2-10-g. sample for 4 hrs. in a  $\text{H}_2\text{O}$  oven gives results comparable to those with the vacuum method.

H. A. LEPPER

The determination of formic acid in fruit juices. WILHELM MÜLLER. *Mil. Lebensm. Hyg.* 13, 320-2 (1922).—It is necessary to run a blank in using the method of the Swiss *Lebensmittelbuch*. The use of  $\text{CaCO}_3$  followed by tartaric acid is recommended to shorten the time on fruit juices but not on sirups.

H. A. LEPPER

The acids of fruits used in jam making. C. F. MUTTELET. *Ann. fals.* 15, 453-5

(1922); cf. *C. A.* **3**, 2716; **16**, 3142.—*Malic acid* was found (g. per 100 cc. of juice) in sour cherries 1.32, Burgundy cherries 1.04, bigarons 0.82, Montmorency cherries 1.61, apples (variety unidentified) 0.40, russet apples 0.49, sour cider apples 0.75, bitter cider apples 0.14, sweet cider apples 0.13, pears 0.30, quince 1.10, green-gages 1.05, mirabelles 0.29, large plums ("quetsches") 0.84. *Citric acid* found was: red gooseberries 2.08, white gooseberries 2.20, black currants 3.50, raspberries 2.12, strawberries (variety unidentified) 1.05, 1.18, Héricart strawberries 1.12. Apricots gave 0.33 malic and 1.75 citric acid, and peaches gave 0.19 and 0.31, resp. Hence, if jams, jellies, etc., from any of the above fruits contain *tartaric acid*, the latter was intentionally added; and if the acidity of such products is due entirely to tartaric acid, they do not contain any fruit juice.

A. P.-C.

**Report on the determination of pectin in fruit and fruit products.** H. J. WICHMANN. *J. Assoc. Official Agr. Chem.* **6**, 34-40(1922).—Collaborative results are reported on the analysis of a strawberry jam contg. added pectin for alc. ppt. (4 methods), pectic acid, ash, S in ash, total S and H<sub>2</sub>O-insol. solids (2 methods). The methods including prepn. of sample are given. The tentative Assoc. method for alc. ppt. gives high results and it is recommended that it be dropped. Results on S in ash indicate that some S is lost in ashing. This is the simplest method of detg. S but not the most accurate.

H. A. LEPPER

**Residue from the manufacture of kaffir beer.** ANON. *J. Dept. Agr. Union S. Africa* **6**, 28(1923).—The wet dregs of "Mayovo," as this residue is termed, give about 25% of air-dried material contg. moisture 11.10, ash 1.00, crude fat 8.6, crude fiber 6.6, crude protein 19.8, sol. carbohydrates 52.9%, nutritive ratio 1:3.6. K. D. J.

**The sweetening of ciders with honey.** A. TRUELLE. *J. agr. prat.* **38**, 458-9 (1922).—A general discussion of honey as a sweetening agent for cider from chem., fermentation, and legal viewpoints. Practical directions are given. W. H. FRY

**The sugars and albuminoids of oat straw.** S. H. COLLINS AND B. THOMAS. *J. Agr. Sci.* **12**, 280-91(1922).—Analytical data are presented to substantiate the view that the percentage of albuminoids of oat straw detrs. the feeding value, and conditions obtaining in England favoring or not favoring production of good straw are pointed out.

R. B. DREMER

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Estimation of water by the apparatus of Meihuizen (Möhs) 7.

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**Baking powder.** L. J. HENDERSON. U. S. 1,413,180, Jan. 23. A baking powder is formed of NaHCO<sub>3</sub> 514, K H tartrate 1486, and desiccated ox serum 1000 parts. The buffer action of the blood serum is stated to regulate the H-ion concn. of cake doughs or the like so as to render the mixt. very effective in securing a full leavening effect for a given amt. of CO<sub>2</sub> evolved.

**Evaporating whey.** H. V. DUNHAM. U. S. 1,443,528, Jan. 30. A blast of air is utilized to prevent overflowing or burning of foam from the whey in an evapg. pan provided with baffle plates.

**Butter substitute.** J. C. SHERMAN. U. S. 1,444,562, Feb. 6. A hard edible fat free from H<sub>2</sub>O, such as hydrogenated cottonseed or peanut oil, is mixed with sufficient dry milk powder to give the mixt. a flavor similar to that of butter.

**Milk albumin and milk sugar.** A. D. FRET. U. S. 1,444,178, Feb. 6. Milk is desiccated under such moderate heating as not to render the albuminous constituents insol. and the sol. albuminous material is then leached out of the dry product with such a limited amt. of H<sub>2</sub>O as to leave most of the milk sugar undissolved.

**Milk cultured with lactic acid bacteria.** W. J. BRUCE. U. S. 1,443,458, Jan. 30.

CaCO<sub>3</sub> is added to pasteurized whole milk which is then inoculated with *Bacillus bulgaricus*, incubated and cooled.

**Apparatus for determining the freezing point of milk.** J. HORTVET. U. S. 1,443,537, Jan. 30. The app. is adapted for rapid cooling of the milk sample to the f. p. by evapn. of a volatile liquid.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

**Retrospect and prospect.** ANON. *Chem. App.* 10, 1-3(1923).—A general review of the difficulties imposed by the war on Ger. chem. industries on account of shortage of metals, fertilizers, fuels, etc., and the prediction that the recovery of Germany depends largely on her chem. industries. J. H. MOORE

**The growing chemical industry of Palestine.** P. E. SPIELMANN. *Chem. Age* (London) 8, 114-6(1923). E. J. C.

**The dollars and cents of careful barrel handling.** M. W. POTTS. *Chem. Met. Eng.* 28, 293-6(1923). **How to save money by proper barrel handling.** *Ibid* 345-8. A problem in barrel storage and how it is solved. *Ibid* 404-7. E. J. C.

**The relation of plant equipment manufacture to chemical industry.** ROBERTS EVERETT. *Chem. Age* (N. Y.) 31, 5-6(1923). E. J. C.

**Condensation by means of a counter-current barometric condenser without air-pump.** EMIL HAHN. *Chem.-Zig.* 46, 1124-5(1922).—The complicated and expensive air-pump may be replaced by a water suction pump. This can be made so as to operate on 7 m. water pressure. The water used cools the air, reducing its vol. and the work required. ERNEST W. THIELE

**Our broadening knowledge of lubrication.** A. E. DUNSTAN AND F. B. THOLE. *Chem. Met. Eng.* 28, 299-302(1923).—A review with a suggested research program. E. J. C.

**Method of test for modified "resistance to emulsification" number of lubricating oils.** W. E. PERDEW, et al. *Proc. Am. Soc. Testing Materials* 22, I, 431-40(1922).—A discussion of various emulsification tests is presented and a proposed method outlined by the sub-committee on emulsification. W. F. FARAGHER

**Chemical valuation of the filler for high-current cable insulation.** J. W. H. VIJTEN-BOOGAART. *Ingenieur* 37, 263-7(1922).—The properties of natural and artificial asphalts which are to be used for elec. machinery, especially for insulating cable connections, etc. Free C, contained in the mass, is undesirable because it decreases the insulating power; it is detd. by extg. the bitumen with C<sub>6</sub>H<sub>6</sub> or CS<sub>2</sub>. It is higher, as a rule, in the artificial asphalt. The C content of an asphalt may be increased by heating. Artificial asphalt, e. g., residue in the distn. of mineral oil, is more stable in this regard than the natural. It is important, therefore, to det. in a definite sample not only its actual C content but also its possible increase, when heated. The inorg. constituents are also to be detd.; they seem to raise the m. p. of the mass; water-sol. inorg. substances decrease the insulating power. The filler should not contain low boiling hydrocarbons, as they may give rise to the formation of bubbles. These volatile constituents are detd. in a special app. by heating with boiling naphthalene. After heating the mass is cooled and its tensile strength is tested in the usual manner by means of a dynamometer. If, owing to the heating, the mass contains gas bubbles its tensile strength will be decreased. To det. the permeability of the filler for moisture a solid layer of the mass is laid on a piece of paper impregnated with phenolphthalein. A column of water made slightly alk. presses against the insulating layer from the other side, producing a red

color on the paper, if there is any permeability. A good filler should be impermeable for at least 240 hrs. to a water column 5 m. high; this is 3 times higher than the water pressure on cables in the coil can ever be. The filler should contain no high-mol. org. acid which can be saponif. and no free  $H_2SO_4$ .  
R. BEUTNER

**Sanitation in the lead working industries.** AGASSE-LAFONT, FEIL AND P. POUILLOT. *Recherches et inventions* 4, 34-40, 56-65(1923).—A description of the manuf. of Pb plates for accumulators, with a discussion of the dangers caused by dust and fumes. Report is given of a detailed study of all employees (96) in one plant (cf. C. A. 16, 2926; Heim, C. A. 17, 586), and recommendations for improving sanitary working conditions are made.  
A. P.-C.

**Pneumonokoniosis of metal polishers.** HEIM, AGASSE-LAFONT, AND P. POUILLOT. *Bull. official direction recherches sci. ind. inventions* No. 35, 562-72(1922).—Tests were carried out in shops not equipped with fans for removing the dust. In a poorly ventilated Ni-polishing shop the air at the height of the workmen (4) contained 10 mg. of dust per  $m^3$  with a trace of Ni. The dust from the floor contained 6.3% Ni and from the work benches 16.5%. The air from 2 brass polishing shops contained, resp., 10 and 30 mg. of dust per  $m^3$  of which a trace and 0.002 mg. were Cu. The dust from the floor contained, resp., 48.9 and 36% Cu, from the work benches near the grindstones 50.8 and 56.3%, and from the benches near the buffers 23.5 and 10.7%. The dust inhaled therefore consists almost entirely of the polishing material, with but traces of metal; but when Pb is involved it gradually causes a latent saturnism. Clinical and radiological exams. on a large no. of workmen are reported.  
A. P.-C.

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Ultimate structure of materials as a cause of their technically important properties (RINNE) 2.

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**Fractional crystallization.** H. V. A. BRISCOE. U. S. 1,443,616, Jan. 30. Mixed solns. such as those contg. both  $KNO_3$  and  $NaNO_3$  are successively subjected to concn. and temp. conditions to promote the crystn. of one only of the compds. and the soln. is cooled to effect crystn. of the sep. substances, each under the conditions favorable to its fractional sepn. from the other compd. In a soln. contg.  $KNO_3$  and  $NaNO_3$ , the  $KNO_3$  may be first crystd. by cooling the soln. to  $15^\circ$  after bringing it to a concn. of  $97^\circ Tw.$  and a temp. of  $39^\circ$  and the  $NaNO_3$  may then be crystd. by cooling the residual soln. to  $52^\circ$  after concg. it to  $120^\circ Tw.$  and bringing its temp. to about  $120^\circ$ .

**Absorbing gases in liquids.** R. B. WOLF. Can. 227,606, Jan. 2, 1923. In the absorption of gases, e. g., production of acid sulfite liquor, the gases are brought into contact with the liquor by counter-current circulation, the resulting liquor is drawn off and brought in intimate contact with strong gases in a blower which is protected from corrosive action of the gas by the presence of the liquor. App. is specified.

**Compressing gases.** W. WILKINSON. U. S. 1,443,550, Jan. 30. O or other gas is compressed in contact with  $H_2O$  and the amt. of  $H_2O$  absorbed by the gas is restricted by an escape valve at the compressor outlet which prevents the pressure from rising above a fixed limit.

**Foam for preventing evaporation of stored liquids.** F. A. HOWARD, G. H. L. KENT, AND J. M. JENNINGS. U. S. 1,443,538, Jan. 30. Evapn. of gasoline or other volatile liquids is prevented by foam from a mixt. contg. glue, starch, glycerol, glucose and  $H_2O$ .

**Recovering phenol vapors with tar oils.** W. RUNGE AND H. A. CURTIS. U. S. 1,440,108, Dec. 26. In recovery of volatile solvents from air by the Bregeat process (C. A. 13, 2983), phenol or cresol vapors which are carried with the spent gas from the absorption medium are recovered by absorption in coal tar neutral "dead oil" which

may be thus satd. with the phenol or cresol sufficiently to constitute a good disinfectant mixt. or which may be used as a source of subsequent sepn. of the PhOH or cresol.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

**Chemical characters of the waters of Angat and Montalban rivers, P. I.** R. H. AGUILAR. *Philippine J. Sci.* 22, 43-53(1923).—Descriptive, with analyses.

R. J. C.

**The sulfated waters of Essex.** J. C. THRESH. *Pharm. J.* 109, 557-8(1922).—Analyses are given of mineral waters from the beds of the London clay. They may show much difference in compn. although obtained by boring in close vicinity. The waters of "Hockley Spa" and of "Vange" are contrasted, the former contg. no  $K_2SO_4$ , no  $Na_2SO_4$ , and less than  $1/2$  of  $MgSO_4$ , as compared with the latter. S. WALDBOTT

**The calculation of the salt content of drinking water from the electric conductivity.** I. M. KOLTHOFF. *Chem. Weekblad* 19, 407-9(1922).—For calcg. the total content of the non-volatile substances of drinking water, the elec. cond. should be multiplied with the factor  $0.71 \times 10^6$ . For calcg. the ash the factor  $0.68 \times 10^6$  and for ash minus  $SiO_2$  the factor  $0.63 \times 10^6$  should be used. The values, thus calcd., agree with those directly detd., in a great number of expts., within 10% in all cases, and within 5% in most cases.

R. BEUTNER

**Zeolites and their commercial applications.** LUCIEN MAUGÉ. *Industrie chimique* 10, 14-8(1923).—A description of zeolites, their manuf., and their uses, particularly for water purification.

A. P.-C.

**Purification of water for industrial use.** S. T. POWELL. *J. Am. Water Works Assoc.* 10, 1-43(1923).—A very complete summary of the various methods recommended and in use for industrial water purification; it includes sedimentation, filtration, lime and soda ash (cold and hot), zeolites as softeners, deconcentration or sludge removal, evapn., degassing by heat, vacuum, and chemicals, and boiler compds. Caustic embrittlement is referred to and especial consideration is given to trouble typical in railroad practice, laundry use, and in the paper, textile, tanning, chemical, brewing and ice mfg. industries.

D. K. FRENCH

**Filters for removing oil from boiler feed water.** L. A. DAY. *J. Am. Water Works Assoc.* 10, 145-6(1923).—Details are given, with cuts, of a filter which is very successful in removing objectionable oil from condensate returning to the boilers.

D. K. F.

**Oxygen absorption by boiler-feed water.** F. C. WIRTZ. *Dé Ingenieur* 37, 444-6(1922).—To det. the  $O_2$  content of the water add 5 cc. 30% NaOH + 2 cc. 50% KI, after 15 min. add concd. HCl and titrate. Pour a layer of mineral oil upon the water to prevent the taking up of  $O_2$  during the detn. The  $O_2$  content of water is increased up to 183% if it falls a distance of only a few cm. in the open atm. A water meter may cause a great increase in the  $O_2$  content, unless it is airtight.

R. BEUTNER

**Drinking water for animals.** L. PAUTET. *L'eau* July 15, 1922, pp. 7; *Water & Water Eng.* 24, 413(1922).—A temp. of 12-14° in winter and 15-18° in summer is recommended.

JACK J. HINMAN, JR.

**Tastes and odors in public water supplies from decomposing organic matter.** F. H. WARING. *J. Am. Water Works Assoc.* 10, 75-87(1923).—Later results seem to confirm the earlier observations (cf. *C. A.* 16, 601).

D. K. FRENCH

**The treatment of sewer water.** LÉONCE FABRE. *Chimie et industrie* 8, 1180-1200(1922).—Various methods are described.

A. P.-C.

**Effect of certain chemicals on the filtration of ripe Imhoff sludge.** P. A. VAN DER



MEULEN and R. O. SMITH. *Ind. Eng. Chem.* 15, 281-2(1923).—Addns. of  $\text{H}_2\text{SO}_4$  first produced a gelatinous cake, then a sharply defined point at which the cake became less gelatinous and filtered more readily. Further addns. again gave a gelatinous cake. The optimum  $p_{\text{H}}$  with  $\text{H}_2\text{SO}_4$  was 4.2.  $\text{H}_2\text{SO}_3$  gave the same results as  $\text{H}_2\text{SO}_4$ , but larger amts. were required to produce the same effect. An application of 6.7 lbs.  $\text{Al}_2(\text{SO}_4)_3$  per cu. yd. of sludge gave a porous cake readily freed from moisture. The odor of the cake was not so offensive as that of the acid cakes. Further addns. of coal ashes gave a somewhat increased wt. of cake over the wt. of ashes used. Clay and burned CaO gave no advantages.

G. C. BAKER

Aeration of sewage of small towns. W. G. CAMERSON. *Contract Record* 36, 900-1(1922); *Pub. Health Eng. Absts.*, Feb. 17, 1923.—Drop manholes are suggested for the partial aeration of sewage of small communities. Where grades prohibit their use water wheels can be placed in the sewers. Efficiency of the wheels can be increased by causing them to operate small air pumps and the air utilized for further aeration.

G. C. BAKER

Effect of non-aeration on the activated sludge process of sewage purification. G. A. H. BURN. 39th Ann. Rept. Provincial Board of Health, Ontario, Canada 1920, 121-9; *Pub. Health Eng. Abstracts* Feb. 24, 1923.—With a 4-hr. stoppage the bacteriol. condition is again normal in 6 hrs. after aeration is resumed. The free  $\text{NH}_3$ ,  $\text{NO}_2$  and  $\text{NO}_3$  are again normal after 7 hrs.; the albuminoid  $\text{NH}_3$  is normal in 3 hrs., and the dissolved O in 2 hrs. O consumed recovery was irregular and Cl was not particularly efficient with the effluent.

G. C. BAKER

Sewage disposal in the small community. W. C. HIRN. *Public Health* (Mich. St. Bd. Health) 11, 34 8(1923).

JACK J. HINMAN, JR.

Collection and incineration of garbage. The Rouen garbage incinerator. H. COURTOTNE. *Bull. soc. ind. Rouen* 50, 319-30(1922).

A. P. COUTURE

Plumbing regulations. GEO. C. WHIFFLE. *Public Health* (Mich. St. Bd. Health) 11, 25-9(1923).—The present state of the "sewer gas" question is discussed.

JACK J. HINMAN, JR.

Typhoid fever. F. G. BOUDREAU. *Public Health* (Mich. St. Bd. Health) 11, 4-16(1923).—Water and milk borne epidemics and their characteristics are discussed.

JACK J. HINMAN, JR.

Atmospheric conditions in industry. H. M. VERNON. *J. Ind. Hyg.* 4, 315-24 (1922); cf. *C. A.* 16, 3151-2.—The kata-thermometer was used in the investigations made in industries where the processes should not interfere with the attainment of the normal standards, and also in workshops where the standards must be lowered because of the nature of the work. A dry Kata standard of 6 is suggested (at 62° F., an air velocity of 14 ft. per min.) when the outside temp. is 70° F. or less, but the standard should be lowered to 5 (at 75° F., velocity of 47 ft. per min.), if the outside temp. is higher. An investigation of 35 factories in the boot and shoe industry showed them to be near the normal standard. The workshops of the printing trade while not as satisfactory as those of the boot and shoe industry were better than those in the pottery manuf. In the cotton weaving industry, and in the laundry trade only a small % came up to the standard. The installation of suitable ventilating fans would have brought them to the standard conditions.

A. A. CHRISTMAN

Total and available calcium hydroxide in hydrated lime (BEHRMAN, PORTER) 7.

Apparatus for heating and purifying water. O. L. FOWLER. U. S. 1,445,134, Feb. 13. The app. comprises superposed chambers through which exhaust steam is passed to heat the  $\text{H}_2\text{O}$ .

**Apparatus for treating water with zeolites.** S. B. APPLEBAUM. U. S. 1,443,892, Jan. 30. The casing contg. zeolitic material is provided with connections for passage of water to be softened, salt soln. for regeneration of the zeolitic material and a float for controlling flow of backwash water through the filter bed.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

**Agricultural chemistry and colloid chemistry.** GEORG WIEGNER. *Kolloid-Z.* 31, 271-5(1922).—A general discussion of the properties of *soil colloids*.

M. S. ANDERSON

**Iroquois County soils.** J. G. MOSIER, S. V. HOLT, E. VAN ALSTINE AND H. J. SNIDER. Univ. of Ill Agr. Expt. Sta., *Soil Rept.* No. 22, 60 pp. **DeKalb County soils.** J. G. MOSIER, H. W. STEWART, E. E. DETURK AND H. J. SNIDER. *Soil Rept.* No. 23, 54 pp. **Adams County soils.** J. G. MOSIER, F. W. WASCHER, W. R. LEIGHTY AND H. J. SNIDER. *Soil Rept.* No. 24, 62 pp.(1922). E. J. C.

**The laterite soils of Formosa Island.** KISABURO SHIBUYA. *Soil Science* 13, 425(1922).—These soils are heavy, red, residual clays, largely of sandstone and shale origin, which have lost the greater part of their sol. constituents by prolonged weathering. Decompn. forces are so active that humus does not accumulate, consequently the soil has both phys. and chem. properties unfavorable for crop production. Tea yields a 60% av. crop, rice a 50% normal yield; other crops, sugar cane, sweet potato, sesame, peanut, etc., yield from 35 to 60% normal amts. Analyses show  $\text{SiO}_2$  58-77,  $\text{Al}_2\text{O}_3$  9-24,  $\text{Fe}_2\text{O}_3$  3.4-8.4,  $\text{FeO}$  1.44-2.25%. All other basic materials are low, also the quantity of  $\text{SO}_2$  and  $\text{P}_2\text{O}_5$ . The colloidal material was sepd. and found to contain approx.  $\text{SiO}_2$  36,  $\text{Al}_2\text{O}_3$  31,  $\text{Fe}_2\text{O}_3$  14%. The color of the soils is due to the degree of oxidation and distribution of the iron rather than the total amt. present. R. BRADFELD

**Organic constituents of the soil.** G. S. FRAPS. Texas Agr. Expt. Sta., *Bull.* 300, 10 pp.(1922).—Detns. are given and comparisons made of the org. C, N, and pentosans in a no. of surface and subsoils. The detn. of org. C throws little light upon the quality of a soil; its % can be judged from the % of N present. The av. % of pentosans increases with the av. N content. Studies of the rate of disappearance in soil of pentosans from various sources showed after 8 weeks a remainder of 7% of the original pentosans from cottonseed meal, 31% from Sudan grass, 61% from rice bran, and 75% from sheep excrement. The amt. of reducing substance, calcd. as sugars, produced by heating soils with dil.  $\text{H}_2\text{SO}_4$ , varied from 0.002 to 0.215% with an av. of 0.058% for 77 soils. No relation could be found between the permanganate-sol. and -insol. N and the results of pot expts. with N on soils. With 21 soils an av. of 10% of the N was dissolved by 0.1 N KOH. P. R. DAWSON

**Influence of the composition of the soil and the fertilization on the nitrogen content and the ash of domestic plants.** J. G. MASCHHAUPT. *Verslag. Land. Onderzoek. Rijkslandbouwraproefsta.* 27, 82-124(1922).—Flax is grown on various soils and with varying fertilization (with either N only or N, P and K or N and K). The N content of the plant is highest on marshy ground. Fertilization has no considerable influence on the compn. of the plant, except K fertilization, which raises the K content of the stem. R. BEUTNER

**The formation of pans in soil.** C. G. T. MORRISON. *Trans. Faraday Soc.* 17, 321-4(1922).—Soil pans may be formed by continued cultivation to a certain depth or by the movement downward of material in the soil. This material may be carried in true soln. or as colloid to a point where it is deposited, acting as a cementing agent on

normal soil particles. Pan formation usually occurs in soils of high quartz content. The org. matter content of most pans is high and the plant food elements are low.

M. S. ANDERSON

**Movement of legume bacteria in soil.** W. C. FRAZIER AND E. B. FRED. *Soil Science* 14, 29-31(1922).—Soy beans were grown in a galvanized box so arranged that water movement through the inoculated area was reduced to a minimum. Under such conditions the legume organism traveled at the rate of 0.1 to 0.2 in. per day. A field test on a large scale confirmed the results of the greenhouse expt. and led to the conclusion that in a soil of the Miami silt loam type soy-bean bacteria spread slowly, if at all, through the soil unless carried by the host plant, or by wind, rain, etc. R. B.

**A tentative outline of the plate method for determining the number of micro-organisms in the soil.** S. A. WAKSMAN. *Soil Science* 14, 27-8(1922).—A brief report of a comm. of soil bacteriologists, recommending certain methods, with the objects of standardizing procedures used in different labs. so that results obtained might be comparable.

R. BRADFELD

**A new method for mechanical analysis of soil and other dispersions.** G. W. ROBINSON. *J. Agr. Sci.* 12, 306-21(1922).—The expression of mech. compn. by means of a continuous curve is discussed. It is shown that a convenient representation will be obtained by showing summation percentage as a function of the logarithm of settling velocity. A method by which the mech. compn. of a soil is derived from detns. of the concn. of a settling suspension for different values of depth/time is given. Various details of manipulation of the method are studied in detail.

R. B. DEEMER

**Note on the mechanical analysis of humus soils.** G. W. ROBINSON. *J. Agr. Sci.* 12, 287-91(1922).—Soils high in org. matter break up into mech. fractions better if oxidized before analysis.  $\text{H}_2\text{O}_2$  proved the best oxidizer; it is used as follows: 10 g. of soil in a 600 cc. beaker are treated with 50 cc.  $\text{H}_2\text{O}_2$  (20 vols.) on a water bath. During the first 30 min. the mass is stirred and after the reaction becomes less violent another 25 cc. of  $\text{H}_2\text{O}_2$  are added. Any froth clinging to the sides of the beaker is washed down with  $\text{H}_2\text{O}$ ; the reaction is usually over in about another 15 min. digestion, though soils extremely high in org. matter need more  $\text{H}_2\text{O}_2$ . 100 cc.  $\text{H}_2\text{O}$  are added; the beaker is removed from the water bath and boiled for 15 min.

R. B. DEEMER

**Variation of nitrate nitrogen and  $p_{\text{H}}$  values of soils from the nitrogen availability plots.** A. W. BLAIR AND A. L. PRINCE. *Soil Science* 14, 9-17(1922).—H-ion detns. on samples of soils collected at 2-wk. intervals for 5 months show only slight variations in  $p_{\text{H}}$  values for a given fertilizer treatment. The  $p_{\text{H}}$  values were consistently lower on the unlimed plots.  $(\text{NH}_4)_2\text{SO}_4$  caused a decided decrease in  $p_{\text{H}}$  on both limed and unlimed plots;  $\text{NaNO}_3$  applications increased the  $p_{\text{H}}$  slightly and lowered the lime requirement detd. by the Veitch method. Bi-weekly nitrate detns. showed considerable variation with the season, being lowest after the crop had been removed in July and August. Limed plots average higher than unlimed plots. Considerable nitrates were found in soils so acid as to inhibit growth of ordinary farm crops. R. BRADFELD

**A possible correlation between the fertility of rice fields and their titration curves.** O. ARRHENIUS. *Soil Science* 14, 21-6(1922).—No close correlation was found between the productivity of certain rice soils in Java and their  $p_{\text{H}}$  values. When titration curves of these soils were detd. the soils having the greater buffer action were the more fertile. A. recommends the use of green manure crops on soils having a low buffer action with applications of lime to bring the  $p_{\text{H}}$  value up to the optimum for the crop. R. B.

**Some investigations on the electrical method of soil moisture determinations.** T. DEIGHTON. *J. Agr. Sci.* 12, 207-29(1922).—Examn. is made of the processes operative and the limits of accuracy of the elec. method of detg. soil moisture. Resistance is found to vary under similar conditions which are most probably due to actual differ-

ences in moisture or other factors. From a study of the effect of distance between the electrodes a min. resistance is indicated. The use of electrode values in computing soil resistances is discussed and criticized. The path of current in the soil is investigated mathematically and the results obtained accord well with the observed facts. The method gives the mean  $H_2O$  content of a vol. of soil somewhat greater than a sphere whose poles are the electrodes. The practical limits of the methods are indicated. At water contents above 10% resistance varies inversely as the square of the moisture contents; while at lower contents 1 and possibly 2 discontinuities appear in the curve, which are reversed in artificial mixts. not contg. colloids. Explanation is advanced in a tentative way.

R. B. DEEMER

**Experiments on the theory of soil acidity.** J. N. MUKHERJEE. *Nature* 110, 732(1922).—In expts. to test M.'s theory (C. A. 16, 4106) of the cause of soil acidity, powd. ppts. of silica adsorbed appreciable quantities of acids so strongly that the adsorbed substance could not be removed with repeated washing and the aq. ext. soon became perfectly neutral. On treatment with neutral KCl soln. the aq. ext. was found to be distinctly acid, the amt. of acid depending upon the amt. of ppt. In the case of acetic and citric acids no trace of acetate or citrate could be detected in this ext. The formation of insol. salts of alk. metals or the replacement of  $H^+$  by metallic ions in complex silicic acids is evidently out of the question. That the entire mol. of acid is not adsorbed was demonstrated by expts. on electroösmosis. As shown by increase in velocity, the negative charge of the pure silica ppt. increased 100 and 50% in the presence of NaOAc and KCl, resp. As was to be expected from the greater mobility of  $H^+$ , acids of the same concn. showed a smaller charge than their salts, but greater than with pure water, so that there is unmistakable evidence of the adsorption of anions. These expts. indicate that it is a question of the kinetic exchange of ions ( $H^+$  or  $Al^{+++}$  in the case of soil acidity) in the 2nd sheet of the double layer, or present as electrically adsorbed.

P. R. DAWSON

**The potential acidity of soils.** O. ARRHENIUS. *Soil Science* 14, 223-32(1922).—A method of detg. the potential acidity of soils from their titration curves is given. A fair correlation was found between fertility and the buffer action of the soils studied. Humus-fertilizing and cultivation are recommended as means of increasing the buffer action of soils. A. recommends the use of titration curves for estg. the lime requirement of soils.

R. BRADFIELD

**Absorption (by soil) of ammonium ions from solutions of ammonium salts and the effect of electrolytes thereon.** B. AARNIO. *Z. Pflanzenernähr. Düngung* [A] 1, 320-5 (1922).—The absorption by soil of  $NH_4$  ions from solns. varies according to the  $NH_4$  salt used for the expt., being approx. the same for  $NH_4Cl$  and  $(NH_4)_2SO_4$  but greater for  $NH_4H$  phosphate. The effect of the addn. of electrolytes on absorption from  $(NH_4)_2SO_4$  and  $NH_4H$  phosphate solns. was also studied. In most cases, absorption is decreased; hydroxyl ions, however, cause increase in absorption. It is held that absorption is influenced according to the effect of the substances present on the degree of dispersion of the absorbent. Electrolytes which flocculate soil decrease absorption, while where a dispersing effect is exerted, absorption is increased. Soil consists both of positively and negatively charged particles and anions are absorbed to some extent as well as cations.

J. C. S.

**Sources of fertilizer constituents in the Philippines.** A. S. ARGUELLES. *Sugar Central and Planter News* 3, 595-8(1922).—Imported com. fertilizers are very expensive. Promising native sources which might be developed advantageously are bat guano, rock phosphates, the ash of the wild banana, of coconut husks, of molasses or of seaweeds, fish, copra cake, cotton seed, lumbang and peanut meals. There are also native legumes useful as cover crops.

F. W. ZERBAN

**Fertilizing value of volcanic ashes.** R. GUILLIN. *J. agr. prat.* **38**, 533-4(1922).—Analyses are given of 2 samples of ash from Santa Maria, Guatemala. The fertility of volcanic deposits is explained on the basis of the easy decompu. of the ash by atm. agencies. W. H. FRY

**Fertilizer experiments with new nitrogen fertilizers.** W. VON KNIERIM. *Mitt. deut. Landw.-ges.* **37**, 654-5(1922).—Urea gave better results on a loamy sand soil than an equiv. amt. of N as  $\text{NH}_4$  sulfate-nitrate or  $(\text{NH}_4)_2\text{SO}_4$ . The effect of varying quantities of N as urea upon the yield of potatoes and forage beets is shown. The season was unfavorable for best results. K. D. JACOB

**The commercial value of nitrogen in the various nitrogenous fertilizers.** CH. HARNIST. *Mém. et compt. rend. travaux soc. ing. civils* **8**, 334-42(1922); *Chimie et industrie* **9**, 109(1923).—Under certain conditions the value of N in  $\text{NH}_3$  fertilizers may be greater than in  $\text{NaNO}_3$ . Ammoniacal compds. are assimilated directly by plants, and are even more suitable than nitrates, but removal of the  $\text{NH}_3$  by the plants causes the acidity of the soil to rise too much. This may be overcome by addn. of a basic substance (e. g.,  $\text{CO}(\text{NH}_2)_2$ ). H. then discusses the value of the N in the various ammoniacal fertilizers (chloride, sulfate, urea); shows the importance of S to the life of plants, the production of chlorophyll and the life of bacteria necessary to plant life; and indicates the improvements which could be brought about in the manuf. of  $(\text{NH}_4)_2\text{SO}_4$  from synthetic  $\text{NH}_3$  by eliminating atm. O by means of S and FeS and transforming  $\text{NH}_4\text{HSO}_4$  into sulfate and S. A. P.-C.

**Nitrogen fertilization of leguminous plants.** SIMMERMACHER. *Mitt. deut. Landw.-ges.* **38**, 12-3(1923).—N in the form of lime-N,  $(\text{NH}_4)_2\text{SO}_4$ , K-NH<sub>3</sub> nitrate,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4$  sulfate-nitrate, and  $\text{NaNO}_3$  had little, if any, beneficial effect upon alfalfa, red clover, peas or horse beans, when applied at the time of sowing or immediately after the first cutting of hay. K. D. JACOB

**Determination of available nitrogen in fertilizers.** R. GUILLIN. *J. agr. prat.* **38**, 415-6(1922).—Chem. methods for the detn. of available N are wrong in principle and do not accord with field experience. The correct method is one that depends upon nitrification in the soil itself. W. H. FRY

**The importance of calcium for plants and soils.** NOLTE. *Mitt. deut. Landw.-ges., Flugblätter* **38**, No. 1, 1-3(1923).—A general discussion. K. D. JACOB

**The phosphoric acid question.** F. O. DIETRICH. *Mitt. deut. Landw.-ges.* **37**, 600-2(1922).—A general discussion on the relation of  $\text{P}_2\text{O}_5$  as a fertilizer to  $\text{K}_2\text{O}$  and N. Phosphoric acid fertilizer practices in England are compared with those in Germany. K. D. JACOB

**Phosphate guano.** P. DE SORNAY. *Rev. agr. Maurie* **1**, 292-6(1922).—Analyses of guano deposits on islands close to Mauritius are given. They vary considerably in compn., but the inorg. portion consists mostly of  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaCO}_3$ . The  $\text{P}_2\text{O}_5$  varies from 2.4 to 30%. The N is usually low, except in fresh deposits. The  $\text{Ca}_3(\text{PO}_4)_2$ , unlike that in rock phosphate, is quite sol. in weak acids and becomes quickly available in the soil. In order to prevent the effect of the  $\text{CaCO}_3$  in the guano on  $(\text{NH}_4)_2\text{SO}_4$  in fertilizer mixts., it is advisable to add acid phosphate. F. W. ZERBAN

**Effect of silicic acid on crop production in the presence of insufficient amounts of phosphoric acid.** O. LEMMERMANN and H. WIESSMANN. *Z. Pflanzenernähr. Düngung* [A] **1**, 185-255(1922).—In working with sand cultures of gramineous, leguminous, and cruciferous plants, increases in yield were obtained by the use of colloidal silicic acid, particularly in the presence of insufficient  $\text{P}_2\text{O}_5$ . In expts. with natural soils, similar results were obtained. With shortage of N or K, the effect of Si is much less. The increases appear to be due to the direct action of silicic acid on plant growth. Si compds. other than colloidal silicic acid gave insignificant or negative results. J. C. S.

Observations on basic slags. A. DEMOLON. *Bull. assoc. chim. suc. dist.* 40, 252-31(1922).—See C. A. 16, 3725. P. R. DAWSON

The influence of potash upon the health of vines and the quality of the wine. L. RAVAZ, G. VERGE, H. LAGATU and L. MAUME. *Prog. agr. vit.* 79, 9-15(1923).—Favorable results with potash on a calcareous soil are reported. P. R. DAWSON

Preparation of peat composts. A. P. DACHNOWSKI. U. S. Dept. Agr., *Circ.* 252, 1-11(1922).—A review of methods for composting peat with stable-manure, sewage, fish scrap and molasses waste from sugar factories. W. H. ROSS

Analysis and sampling of Thomas phosphate. M. J. VAN'T KRUY. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* 26, 96-105(1922).—K. examd. the molybdate, the citrate, the Lorenz, the uranium, and the Grete methods of detn. of  $P_2O_5$  in Thomas slags. The first two methods are not quite reliable; they also require much gas and the use of Pt crucibles. The method of Lorenz, which makes use of a phosphoric acid-molybdate ppt. of const. compn. obtained in a strong acid soln., is recommended. R. BEUTNER

Nitrogen content and specific gravity of liquid manure. G. H. LAGERS. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* 26, 9-18(1922).—The method of detg. N in liquid manure by sp. gr., as recommended by Vogel, is incorrect. R. BEUTNER

The fungicidal properties of certain spray-fluids. III. E. HORTON and E. S. SALMON. *J. Agr. Sci.* 12, 269-79(1922).— $Na_2HAsO_4$  and  $Na_3AsO_4$  and  $Ca_3(AsO_4)_2$  in proper concns. proved fungicidal, while  $CaSO_4$ ,  $CaSO_3$ ,  $CaS_2O_3$ , calcium hydroxyhydrosulfide proved non-fungicidal, though the polysulfide of Ca proved fungicidal. R. B. D.

Probable cause of the toxicity of the so-called poisonous greensand. J. W. KELLY. *J. Agr. Research* 23, 223-8(1923).—Chem. analyses are given of toxic and non-toxic greensand from N. J. and Va. Greensand is a mixt. of glauconite, shell marl and other adhering constituents. Glauconite, from each of the 3 deposits of greensand studied, was found to be toxic to corn seedlings. The toxicity is due to the presence of Fe, Al and Mg in forms readily sol. in weak acid media. The presence of CaO prevents the toxic elements from going into soln. Therefore deposits of greensand like those at Newcastle, Va., and Red Bank, N. J., which naturally contain CaO in the form of shell marl in sufficient quantity to prevent the soln. of the toxic elements, are not toxic to plants. The addn. of CaO to the toxic Courtland, Va. greensand inhibits its toxic effects. F. C. COOK

Bacteria which split nucleoproteins and their significance in the liberation of P in soils (KOCH, OELSNER) 11C. Manufacture of cyanamide (GARAIK) 18. Effect of various inorganic nitrogen compounds, applied at different stages of growth on the yield, composition and quality of wheat (DAVIDSON, LEClerc) 11D.

Granulating cyanide. G. LEFORT DES YLOUSERS. *Can.* 227,478, Dec. 26, 1922. A high instantaneous pressure is exerted on a small mass of raw  $CaCN_2$  intimately mixed with water by oppositely rotated cylinders, at least one of which is perforated.

Insecticide. M. Y. SEATON. U. S. 1,444,430, Feb. 6. A compn. readily miscible with  $H_2O$  for spraying is formed of Mg arsenate with about 4% of Na cassinate or other deflocculating agent which assists in retaining the compn. in a dry adherent film when applied.

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

**New contribution to the analytical study of cider.** P. BALAVOINE. *Mitt. Lebensm. Hyg.* 13, 310-20(1922).—A discussion with tabulated data dealing with the detection of cider in wine based on the ratios of ash consts.

H. A. LEPPER

**The influence of temperature on the fermentation of sparkling wines.** ALFRED MAZZEI. *Rev. vit.* 58, 21-8(1923).—The most favorable temp. for fermentation lies between 13 and 16°, although there is some variation with the strain of yeast. The pressure due to CO<sub>2</sub> tends to inhibit fermentation.

P. R. DAWSON

**Free tartaric acid in the wines of 1922.** FONZES-DIACON. *Prog. agr. vit.* 78, 588-93(1922).—An explanation is offered for the marked excess of tartaric acid with lowered K content of wines of 1922.

P. R. DAWSON

**Tartaric acid and wines with excess of potash in 1921.** FONZES-DIACON. *Prog. agr. vit.* 78, 323-5(1922); cf. *C. A.* 16, 2953.—Expts. show that the addn. of citric acid to a wine abnormally high in K, in which the excess of tartar has pptd., merely raises the total acidity without modifying the content of K and tartaric acid; under similar conditions, the addn. of tartaric acid, while raising the total acidity and tartaric acid content, has no effect upon the content of K. On the other hand, the addn. of sufficient amts. of tartaric acid to a wine contg. excess of K, immediately after vintage and while still supersatd. with tartar, gives a product of normal constitution, with excess of tartaric acid and sufficient acidity to insure good preservation; citric acid does not have this favorable effect.

P. R. DAWSON

**Acetic acid by fermentation of cellulose.** H. LANGWELL. U. S. 1,443,881, Jan. 30. Cellulose, e. g., straw or sulfite pulp "half stuff," is fermented with aeration at a temp. of 60° with addn. of CaCO<sub>3</sub>, glucose, NH<sub>4</sub>Cl, NaCl, K phosphate and enzymes derived from decomposing stable manure, to obtain Ca acetate.

**Potash from distillery waste.** C. HANER, JR. U. S. 1,444,833, Feb. 13. Distillery slop or similar material from which potash is to be recovered is sprayed upward into a combustion chamber of considerable height, with a whirling motion, to form an ash rich in K compds. Cf. *C. A.* 16, 986.

**Glycerol from sugar.** VEREINIGTE CHEMISCHE WERKE AKT.-GES. Ger. 343,321. The fermentation of sugar to form glycerol is carried out with addn. of salts of acid or neutral reaction as well as nutrient salts. As examples of the salts added, FeSO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, NH<sub>4</sub>Cl and CaCl<sub>2</sub> are mentioned. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Na phosphate, K<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> are used as nutrient salts. The addn. of neutral or acid salts increases the yield of glycerol. The yeast is also less harmfully affected than is the case in alk. soln. J. C. S.

**Glycerol from sugar.** VEREINIGTE CHEMISCHE WERKE AKT.-GES. Ger. 347,604. In the formation of glycerol from sugar, the fermentation is allowed to reach its max. intensity and, without interruption of the process, a further addn. of sugar is made together with smaller amts. of yeast and nutrient salts than in the initial mixt. A larger yield of glycerol and a quicker fermentation are thereby obtained. In an example given, the yield of glycerol was 23% of the sugar used.

J. C. S.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**Standardization of digitalis leaves.** C. DE LIND VAN WIJNGAARDEN. *Nederland. Tijdschr. Geneeskunde* 66, I, 2458-9(1922).—The temp. of drying has no distinct influence on the efficiency of digitalis leaves provided it is below 100°, and the leaves are used at

once. If the leaves are to be extd. after a year, they should be dried at no higher temp. than 55°. If the leaves are dried at 30° and extd. after a year a considerable increase of efficiency is observed.

R. BEUTNER

**Analytical methods applicable to the detection of cocaine and its substitutes.**

GERMAINE WALRAND. *J. pharm. Belg.* 4, 785-92, 825-31, 849-53, 869-72(1922).—W. describes and discusses a variety of tests for the identification of cocaine and its substitutes (orthoform or orthococaine, anesthine or benzocaine, novocaine, stovaine, alypine, holocaine) appearing in classical works and the periodicals. The tests for each item are classified. Those for cocaine, for example, are dealt with under the following headings: melting point, rotatory power, reactions which accord with the chem. structure, reactions based on diazotization, reactions based on reducing properties, color reactions, pptn. reactions and microchem. reactions. Tables of physical consts. and analytical data are given.

A. G. DuMEZ

**Matriculation sheets.** A. SCHAMELHOUT. *J. pharm. Belg.* 4, 934(1922).—A monograph intended for the Belg. Natl. Formulary is given for thiosinamine (allylthiourea).

A. G. DuMEZ

\* **Davilla rugosa, a medicinal plant of Brazil.** G. BATTA AND C. GRNOT. *J. pharm. Belg.* 5, 1-3, 17-21(1923).—The prepn. of *Davilla rugosa*, commonly known as "Cipó do Cabodô" or "Capa Homen," used for medicinal purposes is a soft ext. prepd. by exhausting the leaves with H<sub>2</sub>O and evap. off the greater part of the solvent. The ext. is said to exert a local analgesic and vasoconstrictive action, and to give excellent results in the treatment of orchitis, epididymitis hemorrhoids, phlebitis and varices. The powd. leaves analyzed: moisture 12.1%; ash 9.29, 9.26, 9.10%; sugar calcd. as glucose, 9.23% before inversion, 9.61% after inversion; tannin 3.18, 3.36% by the Cu acetate method, 4.36% by Proctor's method, 2.09% by the Ferdinand Jean method and 3.12% by the hide powder method. Alkaloids could not be detected. A. G. DuM.

**Matriculation sheets.** A. SCHAMELHOUT. *J. pharm. Belg.* 5, 12, 28, 48, 64(1923).—Monographs intended for the Belg. Natl. Formulary are given for UO<sub>2</sub>(OAc)<sub>2</sub>·2H<sub>2</sub>O, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Zn(CN)<sub>2</sub>, vanillin, Zr<sub>3</sub>P<sub>2</sub>, SrBr<sub>2</sub>·6H<sub>2</sub>O.

A. G. DuMEZ

**Method for rendering basic medicaments penetrable to the skin.** F. ESCHBAUM. *Ber. pharm. Ges.* 32, 274-8(1922).—Alkaloids, notably quinine, hydrocupreine, veratrine, antipyrine and pyrimidine, were converted into their corresponding oleates or stearates, and the latter thereupon dissolved in oils or fats to yield permanent solns. (liquid or salve consistency), which applied to the skin gave reactions showing absorption of alkaloid.

W. O. E.

**Simplification or chemical control methods of the German Pharmacopoeia.** H. THOMS. *Ber. pharm. Ges.* 32, 301-10(1922).—A discussion of some suggested changes.

W. O. E.

**Filling powder capsules.** R. STEINBRUECK. *Ber. pharm. Ges.* 32, 311-12(1922).

W. O. E.

**Constituents of some Indian essential oils.** J. L. SIMONSEN AND M. G. RAU. *Indian Forest Records* 9, 1-36(1922).—I. *Essential oil from the oleo-resin of Pinus Khasya.*—The oil is superior in quality to that from *P. longifolia* and quite equal to Am. turpentine; it contains *d*- $\alpha$ - and *d*- $\beta$ -pinene, while from the higher boiling fraction longifolene was isolated, identical in all respects with the sesquiterpene present in *P. longifolia*. II. *Essential oil from the oleo-resin of Pinus excelsa.*—The constituents *d*- $\alpha$ -pinene (87.9%), *d*-terpineol, a bicyclic sesquiterpene C<sub>15</sub>H<sub>26</sub>, and a small quantity of a satd. hydrocarbon of the compn. C<sub>11</sub>H<sub>14</sub> were isolated. III. *Essential oil from Cedrus deodara, Loudon* (cf. C. A. 10, 3135).—*p*-Methyl- $\Delta^3$ -tetrahydracetophenone was sepd. in the pure state and identified by means of the semicarbazone, oxime and dibromoöxime. Neither the sesquiterpene nor the sesquiterpene alc. could be identified



since they yielded no cryst. derivs. IV. *Essential oil from Andropogon juarancusa*, Jones.—The oil contained approx. 77% of *d*-piperitone ( $\Delta^1$ -*p*-menthene-3-one). V. *Essential oil from the seeds of Zanthoxylum alatum*, Roxb.—The oil consisted in large part (over 85%) of the hydrocarbon *l*- $\alpha$ -phellandrene, a small quantity of linalool, and an unidentified sesquiterpene. VI. *Essential oil from the seeds of Zanthoxylum acanthopodium* D. C.—In addition to verifying the findings of Schimmel (*Schimmel Ber.* 1900, 62) with respect to the presence of dipentene, *d*-linalool, and Me cinnamate, S. and R. isolated *l*- $\alpha$ -phellandrene and a small amt. of an aldehyde or ketone, cinnamic acid and a mixt. of fatty acids consisting probably of caproic, caprylic and enanthic acids. VII. *Essential oil from the seeds of Zanthoxylum Budrunga*, Wall.—The oil appears to resemble that described by Semmler (*C. A.* 6, 233) and purporting to come from *Z. alatum*; it contains *l*-sabinene, a terpene not previously found in nature, likewise in small quantity a hydrocarbon and an alc.

W. O. E.

Chemical structure of santoperonin. A. MARX. *Pharm. Ztg.* 68, 7(1923).—Polemical. Cf. *C. A.* 15, 3723.

W. O. E.

Pharmacopeia Japonica IV. F. DIETZE. *Pharm. Ztg.* 68, 7-8(1923).—A review.

W. O. E.

History of capillary analysis in pharmacy. C. WACHTEL. *Pharm. Ztg.* 68, 36 (1923).

W. O. E.

Artificial Carlsbad salt. KLUT. *Pharm. Ztg.* 68, 37(1923).

W. O. E.

Bakers' yeast as a medicament. M. BARSICKOW. *Pharm. Ztg.* 68, 49(1923).—Attention is directed to the danger underlying certain modern propaganda advocating the use of fresh bakers' yeast as a material rich in vitamins.

W. O. E.

Essential oils from Tonkin and Annam. JEAN GATTEFOSSÉ. *La Parfumerie moderne* 15, 89-90(1922).—Star anise oil from the fruits and flowers of *Illicium verum* has  $d_{20}$  0.983,  $\alpha_D$   $-0^{\circ}8'$ ,  $n_D^{20}$  1.5546, ester no. 9.33, Ac no. 42.93, solidification point  $9^{\circ}$ , m.  $13.5^{\circ}$ . Pompelmus oil from *Citrus decumana*, obtained by distn., has  $d_{15}$  0.853,  $\alpha_D$   $+97^{\circ}$ ,  $n_D^{20}$  1.4742, ester no. 13.62, Ac no. 44.23, citral content 26% (?). Basilicum oil has  $d_{20}$  0.936,  $\alpha_D$   $+4^{\circ}8'$ ,  $n_D^{20}$  1.4942, ester no. 20.9, Ac no. 111.06. Camphor oil from young branches has  $d_{15}$  0.936,  $n_D^{20}$  1.4704, ester no. 15.67, Ac no. 64.21. Essential oil from *Litsaea citrata* (May-chang oil) has  $d_{20}$  0.866,  $\alpha_D$   $+20^{\circ}2'$ ,  $n_D^{20}$  1.4620, ester no. 7.65, Ac no. 153.07, citral content 8.15%. *Cathetus fasciculata* yields a yellow essential oil having  $d_{15}$  0.885,  $\alpha_D$   $-6^{\circ}5'$ ,  $n_D^{20}$  1.4790, ester no. 7.47, Ac no. 53.20, aldehyde content 5.2%, also a green oil having  $d_{20}$  0.886,  $\alpha_D$   $-0^{\circ}6'$ ,  $n_D^{20}$  1.4772, ester no. 10.45, Ac no. 50.21. Beu-ring oil from the leaves of *Alpinia* or *Zingiber*, sp., has a pleasant tar-like odor,  $d_{15}$  0.902,  $\alpha_D$   $+8^{\circ}8'$ ,  $n_D^{20}$  1.4884, ester no. 10.92, Ac no. 123.57. Sau-mon oil from *Cunninghamia sinensis* has a strong odor like terpineol,  $d_{15}$  0.957,  $\alpha_D$   $-23^{\circ}6'$ ,  $n_D^{20}$  1.4932, ester no. 21.09, Ac no. 120.02. Pe-mon oil from *Fokienia Hodginsii* has  $d_{15}$  0.913,  $\alpha_D$   $+13^{\circ}$ , ester no. 23.14, Ac no. 188.34.

J. C. S.

Essential oil of juniper from Cyrenaica. V. MASSERA. *Riv. Ital. ess. profumi* 4, 23-4(1922).—A sample of essential oil of juniper from Cyrenaica had  $d_{15}$  0.8715,  $[\alpha]_D$   $+6^{\circ}$ ,  $n_D^{20}$  1.4732, acid no. 0.54, esterification no. 4.91, Ac no. 11.92.  $\alpha$ -Pinene and cadinene were present. A sample from another locality had similar properties.

J. C. S.

Essential oil of violet roots. A. GORIS AND CH. VISCHNIAC. *Roure-Bertrand Fils Bull. Sci. Ind.* [iv] 3, 1-8(1921).—The roots of violet (*Viola odorata*) contain an essential oil and a glucoside. The ethereal oil is a salicylic ester. The amt. of glucoside is small. It is acted on by an enzyme contained in the root with the formation of an essential oil of strong odor.

J. C. S.

Essential oils. ROURE-BERTRAND FILS. *Roure-Bertrand Fils Bull. Sci. Ind.* [iv] No. 3, 14-19(1921); cf. *C. A.* 14, 3751, 3752.—Boldo leaf oil, the essential oil from

the leaves of *Peumus Boldus*, Mol., has  $d_{17}$  0.9318,  $d_{15}$  0.9334,  $[\alpha]_D$   $-0.14^\circ$ , acid no. 1.87, sapon. no. 14.87, it contains 30% of cineole. The oil from the distn. water has  $d_{15}$  0.9323, acid no. 3.73, sapon. no. 26.13, Ac no. 142.18. It has a different odor from that of the first oil and contains 15% of phenols. Patchouli oil (Sumatra) from the leaves has  $d_{15}$  0.9689,  $[\alpha]_D$   $-52^\circ 4'$ , acid no. 1.2, sapon. no. 7.9, Ac no. 26.13. Patchouli oil from the stems has  $d_{15}$  0.9739,  $[\alpha]_D$   $-54^\circ 8'$ , acid no. 8.7, sapon. no., 10.0. J. C. S.

**Two Indo-Chinese oils.** ROURE-BERTRAND FILS. *La Parfumerie moderne* 14, 151 (1921).—Pagoda corn oil has a similar odor to those of geranium and bergamot. It has  $d_{20}$  0.920,  $[\alpha]_D$   $+56^\circ 8'$ ,  $n_D^{20}$  1.4870, sapon. no. 13.25, Ac no. 139.13, free alc. 38.20%. Limonene and geraniol are present (cf. preceding abst.). Annam brier oil has an odor like that of cajuput oil. It has  $d_{15}$  0.886,  $[\alpha]_D$   $-0.6^\circ$ ,  $n_D^{20}$  1.4772, ester no. 10.45, Ac no. 50.21, free alc. 11.27%. It is probably obtained from *Cathetus fasciculata*, Lour. J. C. S.

**Lactic and proteolytic ferments.** G. MEZZADROLI. *Boll. ass. ital. ind. zucchero* 15, 9-13 (1922); *Chimie et industrie* 9, 54 (1923).—Lactic ferments act as a disinfectant and coagulant for putrefactive bacteria owing to the lactic acid and have a caseolytic action by solubilizing the pptd. proteins. Certain com. preps. sold in tablet form rapidly lose all activity. M. tried directly broth cultures of the ferments: 20 cc. stopped diarrhea in 6 hrs. The proteolytic germs must cause an increase in the concn. of agglutinins. A. P.-C.

**The standardization of disinfectants.** T. BOKORNY. *Chem.-Ztg.* 46, 764-5 (1922).

F. W. TANNER

**Assay of some official tablets.** M. FRANÇOIS. *J. pharm. chim.* 26, 330-42 (1922).—Methods are given for characterizing gum tragacanth, gum arabic and carmine in tablets. The assay of the tablets of  $KClO_3$ ,  $Na_2B_4O_7$ ,  $NaHCO_3$ , S, santonin, and the unofficial chocolate-santonin (B) is discussed in detail. That of santonin (A) (cf. C. A. 16, 3730) is based on the soly. of its Ca compd. in hot 95% EtOH, and in  $H_2O$ , pptn. of A by HCl, and its soly. in  $CHCl_3$ . It is characterized by a color test when melting it with KOH on a slide. To det. the amt. of A in B, proceed as before, but filter off the fat before pptg. with HCl. A recent work of M. Chataigner (Bordeaux) on the assay of medicinal tablets is referred to. S. WALDBOTT

**Compound of antipyrine with xanthidrol.** R. FABRE. *J. pharm. chim.* 26, 372-8 (1922); cf. C. A. 16, 4299.—Equimol. amts. of antipyrine (A) and xanthidrol in AcOH soln. slowly form a cryst. compd.  $C_{24}H_{20}N_4O_2$ , m. 178-179°, insol. in  $H_2O$ , very little sol. in Et<sub>2</sub>O, sol. in warm MeOH, EtOH, AcOH and  $C_6H_6$ . The possible presence of A in urine is a source of error in the *detn. of urea* by Fosse's method, but exact results are obtained on previously pptg. A from the urine with Tanret's reagent. S. WALDBOTT

**The phosphates of strychnine.** J. ROUILLOT. *J. pharm. chim.* 26, 406-15 (1922).—Only the mono- and dibasic phosphates of strychnine exist. Both are easily obtained by the direct union of the acid and the base, the monobasic (A) by the aid of  $H_2O$ , the dibasic (B) with 80% EtOH, which is analogous to the prepn. of the arsenates of strychnine (J. B., *Arsenates, methylarsenates and phenylarsenates of strychnine*; Thesis, Paris, 1922). Salt A +  $2H_2O$ , sol. in 25 parts  $H_2O$  ( $15^\circ$ ), little sol. in cold EtOH, nearly insol. in Et<sub>2</sub>O and  $CHCl_3$ ;  $[\alpha]_D$   $-23^\circ$ . Salt B +  $9H_2O$ , little sol. in cold  $H_2O$  with partial decompn. into A and insol. strychnine; nearly insol. in Et<sub>2</sub>O and  $CHCl_3$ ;  $[\alpha]_D$   $-43^\circ 13'$ . S. WALDBOTT

**Colloidal kaolin.** A. WHITE-ROBERTSON. *Pharm. J.* 109, 396-7 (1922).—A good kaolin for medicinal use should contain no toxic matters, should yield no bacterial growth on culture, and should be quite free from alkali or inorg. salts, which would cause flocculation, destroying its colloidal properties. Pure colloidal kaolin will imbibe and retain a large amt. of  $H_2O$  and absorb toxins on its emulsoid surfaces far better than the best

levigated ordinary kaolin. Thus it becomes valuable in reducing intestinal catarrh and removing chronic intestinal stasis. A combination of colloidal kaolin with mucilage of tragacanth is singularly resistant to flocculation, even in presence of  $\text{H}_2\text{SO}_4$  or  $\text{NaCl}$ .

S. WALDBOTT

**Lac Magnesiae.** C. E. CORFIELD. *Pharm. J.* 109, 416-7, 453, 478-9(1922).—To obtain a sufficiently opaque, non-pptg. milk, C. incorporates the light  $\text{MgO}$  with the  $\text{NaOH}$  soln. before adding it to the  $\text{MgSO}_4$  soln. The amt. of light  $\text{MgO}$  used is 7 times the  $\text{MgO}$  to be pptd. as  $\text{Mg}(\text{OH})_2$ .

S. WALDBOTT

**Indian oil of turpentine.** H. C. T. GARDNER. *Pharm. J.* 109, 3, 430(1922); P. H. GUEST. *Ibid.* 411.—Ga. asserted genuine Indian oil yielded only 70-74% instead of the required 90% of distillate between  $154^\circ$  and  $170^\circ$ . Gu. shows that present Indian oils meet the specifications for Am. oils although another analysis by Ga. shows 88% distg. at  $200^\circ$ .

S. WALDBOTT

**The arsenic and lead limits of the British pharmacopeia.** P. A. W. SELF. *Pharm. J.* 109, 464(1922).—A table showing the approx. yearly ingestion of As and Pb for each of 79 chemicals indicates that while in a few cases the retention of existing limits seems desirable, in many other instances the limits are absurdly stringent. However, a lowering of the standard might invite the importation of inferior foreign chemicals.

S. WALDBOTT

**The new Japanese pharmacopeia.** ANON. *Pharm. J.* 109, 559-62, 584-6(1922).—An historical review is given, and 15 articles dealing exclusively with *Japanese drugs* are quoted in full, in addition to 11 monographs on other subjects, e. g., Alcohol absolute, Diastasa, Argentum colloidal, Tuberculinum, etc.

S. WALDBOTT

**Note on hydrastine.** D. B. DORR. *Pharm. J.* 109, 607(1922); *Chemist & Druggist* 97, 779-80(1922).—Com. hydrastine m. at  $130-135^\circ$  (usual m. p.  $132^\circ$ ); but when pptd. with  $\text{NH}_4\text{OH}$  from soln. in acid and recrystd. from  $\text{EtOH}$  the base m. at  $145^\circ$ . The  $\text{HCl}$  salt is said to m. at  $116^\circ$ , but the m. p. of the air-dry salt is indefinite and variable. After it is dried near  $100^\circ$ , it will m. at  $168^\circ$ , with some decompn.

S. WALDBOTT

**Tincture of iodine; French codex, 1920.** G. WALKER. *Pharm. J.* 109, 609-10(1922); *Chemist & Druggist* 97, 944(1922).—W.'s formula of 1920 (C. A. 15, 924) (I 40 grains, KI 10 grains, 90%  $\text{EtOH}$  1 fluid ounce) has the same strength in I as the French Pharm. 1908; the KI content offsets the reduction in  $\text{EtOH}$  from 95% to 90%. The 1920 Codex formula has 25% I less than that of 1908, and 12% KI more than W.'s formula. To obtain the same effect of its I content, the dose must be increased about 25%.

S. WALDBOTT

**Note on potassium iodide in tincture of iodine.** THOMAS STEPHENSON. *Pharm. J.* 109, 610(1922).—The presence of KI in the tincture of the French Codex renders the tincture unsuitable for administering large and progressive doses of I in special cases (cf. C. A. 15, 924). Without KI, large doses of I may be supported without harm, because less toxic org. compds. are probably formed in the system, while KI would soon produce iodism. A return to the Edinburgh tincture of 1 grain per 16 minims is suggested, also a combination of the tincture with milk.

S. WALDBOTT

**Tincture of myrrh in mouth wash.** DAVID MCGHER. *Pharm. J.* 109, 610(1922).—Alum and  $\text{KClO}_3$ , added as ingredients to a milky mixt. of tincture of myrrh and  $\text{H}_2\text{O}$ , cause immediate clotting. To obtain a satisfactory lotion, rub 3.0 g. of myrrh gum resin with 62 cc.  $\text{H}_2\text{O}$  into an emulsion, then add to it a soln. of alum and  $\text{KClO}_3$ , 3.5 g. of each, in 108 cc.  $\text{H}_2\text{O}$ , shake well and add to the mixt. 15 cc. of 90%  $\text{EtOH}$ .

S. WALDBOTT

**Note on cypress oil.** E. M. HOLMES. *Pharm. J.* 110, 107-8(1923).—The properties of oil from various *Cypressus* are given in detail.

S. WALDBOTT

**Notes on crystallized Karlsbad salt.** L. BACHLER. *Schweiz. Apoth. Ztg.* 60,

529-32(1922).—The com. artificial salt, crystd., is mainly  $\text{Na}_2\text{SO}_4$  with small amts. of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  and traces of  $\text{NaCl}$ . Effloresced salts contain more  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  and have an unduly strong alk. taste. The compn. of natural crystd. salt is  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  89.4,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  10.3,  $\text{NaCl}$  0.3%, no  $\text{NaHCO}_3$ ; while Ekkert (*Chem.-Ztg.* 1905, 1315) records for the *powdery*, genuine salt 34%  $\text{NaHCO}_3$  (obtained by satn. with  $\text{CO}_2$ ) and 18%  $\text{NaCl}$ . S. WALDBOTT

**Adonis aestivalis L., summer adonis.** HANS KIEFFER. *Schweiz. Apoth. Ztg.* 60, 562-6(1922).—Injectable preps. of this old domestic remedy are used as a cardiac and diuretic, being more rapidly active than digitalis, and non-cumulative. By judicious use of solvents, K. obtained 0.218% of the saponin-like glucoside *adonin*, (*B*) sol. in  $\text{H}_2\text{O}$ ,  $\text{CHCl}_3$ ,  $\text{EtOH}$ , nearly insol. in  $\text{Et}_2\text{O}$  and petr. ether. It is pptd. by tannic acid, also by picric acid and Mayer's reagent, and concd.  $\text{HNO}_3$  produces indigo blue (cf. N. Kromer, *Arch. Pharm.* 234, 452(1896)). It is probably identical with *B* obtained by Tahara from *Adonis amurensis*, but is 150 times weaker as a cardiac than *adonidin* obtained by Cervello (1880+) from *A. vernalis*, and which Fockelmann (*C. A.* 6, 2671) showed to consist of a mixt. of neutral adonidin and the more toxic *adonidic acid*. Since *A. aestivalis* has a much weaker therapeutic action than *A. vernalis*, its substituting the latter should not be permitted. K. gives the detailed characteristics of fluid ext. of *Adonis aestivalis* as a basis of comparison between the 2 species. S. WALDBOTT

**The assay method of morphine of the new Japanese pharmacopeia.** A. JERMSTAD. *Schweiz. Apoth. Ztg.* 60, 649-51(1922).—The lime method used employs only 5 g. of opium for 100 cc.  $\text{H}_2\text{O}$ , and hematoxylin is the indicator. The values obtained by this method in 3 detns. of morphine in 1 sample were not uniform, as only 2 g. of opium are utilized for pptn.; the results were lower than those obtained by the Helfenberg-J. method (*C. A.* 15, 291, 730, 2337), as some morphine remains in soln. S. WALDBOTT

**The alkaloidal contents of Macedonian and Persian opium.** A. JERMSTAD. *Schweiz. Apoth. Ztg.* 60, 691-4(1922).—Examn. of 2 special samples (*M* and *P*) gave: morphine 13.87% (*M*), 10.69% (*P*); narcotine, resp., 4.67, 11.26; codeine 2.10, 3.23; meconic acid 5.96, 5.58;  $\text{H}_2\text{O}$  7.56, 7.99; ash 3.16, 2.32;  $\text{H}_2\text{O}$ -sol. 61.95, 64.43;  $\text{EtOH}$ -sol. 66.64, 70.67%. The results agree with those for Turkish opium except that narcotine in *P* is very high. The aq. solns. had the usual acid reaction; samples with alk. reaction (probably caused by bacteria) give much lower results in morphine by the Helfenberg method (Giuseppe Biscaro, *C. A.* 15, 2525). S. WALDBOTT

**Indian Mahwa.** A. LENDNER. *Schweiz. Apoth. Ztg.* 60, 713-9(1922); cf. *C. A.* 8, 1850; 15, 2148.—A detailed description is given. Mahwa consists of the fallen flowers of *Ilupe latifolia*, Engler, while *I. malabarorum*, with smaller flowers, shows different anatomical characters. L. isolated a new species of yeast, *Zygosaccharomyces mahwae*, from a culture in sterilized must, into which some of the drug was placed. S. W.

**Fifty years in the service of pharmacy and natural science.** A. TSCHIRCH. ANON. *Schweiz. Apoth. Ztg.* 60, 730-9, 742-60(1922).—A complete list of T's papers and addresses. S. WALDBOTT

**Pharmacopoeial questions regarding galenical preparations.** L. ROSENTHALER. *Schweiz. Apoth. Ztg.* 61, 25-9(1923).—As to tinctures, percolation yields more extractive than maceration; for tincture of cinchona, the process of Pharm. Ital. III gave intermediate results (H. Frerichs). As to fluidexts., Pharm. Helv. IV requires complete extn., except that 0.5% less alkaloid is allowed for cinchona fluidext. This requirement cannot be attained (R. Schreiber, *C. A.* 8, 201), owing to adsorption in the drugs (Palme and Winborg, *C. A.* 11, 2528). Fluidexts. (1:1) being supersatd. solns. tending to ppt., R. recommends preps. having the ratio of 1:2 (drug:ext.). To conserve galenical preps., R. recommends sterilization, e. g., of drugs for tinctures, with boiling  $\text{EtOH}$ ; or heating the finished prepn. S. WALDBOTT

**Dimethylaminoantipyrine (pyramidone).** K. SIEGFRIED. *Schweiz. Apoth. Ztg.* 61, 37-8(1923).—In 3 com. samples, showing irregular m. p., Et<sub>2</sub>O left 10% of an insol. residue which proved to be antipyrine. S. WALDBOTT

The vitamins and the vitamin bunk (LYTHGÖR) 12. Esters of anisic acid (RAD-CLIFFE, BRINDLEY) 10.

**Compound of silver iodide and protein substances.** T. SMITH. *Can.* 227,848, Jan. 9, 1923. A germicidal product contg. AgI, oxidized protein substance and an un-oxidized protein substance sol. in cold water is prepd. by treating freshly pptd. Ag<sub>2</sub>O with a soln. of sol. protein to reduce the oxide to metallic Ag and to oxidize the protein and then treating with I.

**Isopropylallylbarbituric acid.** E. PREISWERK. U. S. 1,444,802, Feb. 13. Isopropylallylbarbituric acid is formed by reaction between the Na salt of isopropylbarbituric acid and allyl bromide. It forms colorless crystals, m. 137-8°, is difficultly sol. in H<sub>2</sub>O, easily sol. in alc. and comparatively sol. in ether, easily sol. in cold CHCl<sub>3</sub> and in aq. soln. is neutral to litmus paper.

**Animal amylase.** R. KERN and G. JENNY. U. S. 1,444,250, Feb. 6. Stable active amylase preps. are obtained from salivary glands, pancreas or the like by evapp. an aq. amylase ext. at a low temp. with Na phosphate or Na sulfate together with gum arabic or other protective colloid.

**A solid water-soluble formaldehyde preparation.** ROBERT COHN. *Ger.* 345,145. Ca lactate is dissolved in 35% CH<sub>2</sub>O soln. at about 90°. The white, cryst. mass obtained on cooling contains CH<sub>2</sub>O in the unpolymerized state and readily sol. in water. The product contains 12-14% of CH<sub>2</sub>O. It may be used in pharmaceutical preps.

J. C. S.

**Aromatic arseno compounds.** ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH. *Holl.* 6352. Aminophenylarsinic acids or aminophenylarsenoxides, unsubstituted in the aromatic nucleus, in which a H atom of the amino group is replaced by an acyl-arylamino group of the compn. —CHR.CO.NHR<sub>1</sub> (R = alkyl, aryl, or H; R<sub>1</sub> = aryl with one or more acid groups such as hydroxyl, sulfonamide, carboxyl, or sulfonic acid) are reduced by ordinary methods to corresponding arseno compds. Phenylglycyl-*m'*-aminophenol-*p*-arsinic acid is reduced by H<sub>3</sub>PO<sub>2</sub> and HI to the corresponding *arseno compd.*, which is a yellow powder, m. 180-190°. The *dihydrochloride* forms a light yellow powder, m. about 130°, which can only be kept in sealed vessels in the presence of indifferent gases, or in a vacuum. Phenylglycyl-*m'*-aminophenol-*p*-arsenoxide, AsO.C<sub>6</sub>H<sub>4</sub>.NH.CH<sub>2</sub>.CO.NH.C<sub>6</sub>H<sub>4</sub>.OH, is prepd. by reduction of the corresponding arsinic acid with SO<sub>2</sub> and HI. It is a white powder with m. p. above 200° after softening at 130°. Phenylglycylanthranilic acid-*p*-arsenoxide, AsO.C<sub>6</sub>H<sub>4</sub>.NH.CH<sub>2</sub>.CO.NH.C<sub>6</sub>H<sub>4</sub>.CO<sub>2</sub>H, is similarly prepd. The compds. have therapeutic uses in trypanosome and spirochete infections.

J. C. S.

**Aromatic aminoarsonic acids.** ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH. *Holl.* 6581.  $\alpha$ -Halogenacylamides of the compn. X.CHR.CO.NR<sub>1</sub>R<sub>2</sub> (where X = halogen, R = alkyl, aryl or hydrogen, R<sub>1</sub>, R<sub>2</sub> = alkyl, aryl, substituted aryl, or hydrogen) are allowed to act on aminophenylarsonic acid, its homologs, its derivs. (substituted in the nucleus), or the salts of these compds. *p*-Phenylglycylamidoarsonic acid, C<sub>6</sub>H<sub>4</sub>-(AsO<sub>2</sub>H<sub>2</sub>)<sup>1</sup>-(NH-CH<sub>2</sub>-CO-NH<sub>2</sub>)<sup>4</sup>, is obtained by the action of chloro- or iodo-acetamide on the Na salt of *p*-aminophenylarsonic acid; it forms colorless crystals, m. above 280°. The sodium salt forms colorless masses of crystals. By treating an alk. soln. of *p*-aminophenylarsonic acid with chloroacetylcarbamide, *p*-phenylglycylcarbamidoarsonic acid, C<sub>6</sub>H<sub>4</sub>-(AsO<sub>2</sub>H<sub>2</sub>)<sup>1</sup>-(NH-CH<sub>2</sub>-CO-NH-CO-NH<sub>2</sub>)<sup>4</sup>, is obtained. *p*-Phenyl-

*glycinearsonic acid* is formed from this acid by hydrolysis; it m. above 280°. The sodium salt contains two mols. of water of crystn. From  $\alpha$ -chloroacetyl-methylcarbamide and *p*-aminophenylarsonic acid, *p*-phenylglycylmethylcarbamidoarsonic acid,  $C_6H_4(AsO_3H_2)(N \cdot H \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot NH \cdot CH_3)^4$ , is obtained; it forms colorless crystals, m. 232°. *p*-Phenylglycylanilinoarsonic acid, prepd. similarly, iodoacetanilide being used, forms a cryst. mass. *p*-Phenylglycyl-*m'*-aminophenylarsonic acid is prepd. by the action of 3 *N*-chloroacetyl-amino-1-hydroxybenzene on *p*-aminophenylarsonic acid in alk. soln. It forms small plates, m. above 230°.

J. C. S.

**Benzyl *p*-aminobenzoate.** SOCIÉTÉ POUR L'INDUSTRIE CHIMIQUE À BÂLE. Swiss 90,587. Comps. contg. a *p*-nitrobenzoyl group are benzylated and the resulting benzyl *p*-nitrobenzoate is reduced. *E. g.*, dry HCl is passed into a benzyl alc. soln. of *p*-nitrobenzoic acid, or *p*-nitrobenzoates are warmed with benzyl chloride in aq. soln., or *p*-nitrobenzoyl chloride is heated with benzyl alc. under a reflux condenser. Benzyl *p*-nitrobenzoate is cryst. It gives, by reduction with iron and dil. HCl, benzyl *p*-aminobenzoate (cf. Shonle and Row, *C. A.* 15, 1528), which forms white needles, m. 90°. It acts as a local anesthetic.

J. C. S.

**Morphine allyl ether.** GEORG VON KERESZTY and EMIL WOLFF. Ger. 343,055. A soln. of an alkali metal compd. of morphine is allowed to react with an alc. soln. of an allyl arylsulfonate. By the action of Na morphine on allyl benzenesulfonate, *allyl morphine ether* is obtained; it forms a *hydrochloride* (+1H<sub>2</sub>O), which m. 129–31° when heated quickly, or 130–2° if heated slowly. The free base m. 67–8°. It has therapeutic uses.

J. C. S.

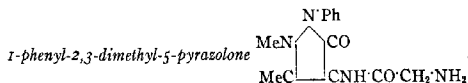
**An unsaturated ether of *p*-dihydroxydiphenylacetamide.** SOCIÉTÉ ANON. POUR L'IND. CHIM. À BÂLE. Swiss 91,728. *p*-Aminophenyl allyl ether is condensed with *p*-acetylaminophenyl allyl ether in the presence of P compds. such as P halides, P<sub>2</sub>O<sub>5</sub>, POCl<sub>3</sub>, or POBr<sub>3</sub>, with benzene or toluene as diluting agents. The *diallyl ether* of *p*-dihydroxyphenylacetamide thus obtained forms colorless crystals, m. 85–6°. The *hydrochloride* is cryst., m. 152–3°. This product has a more powerful local anesthetic action than the corresponding satd. ethers.

J. C. S.

**A derivative of pyridine-3-carboxylic acid (nicotinic acid).** SOCIÉTÉ POUR L'IND. CHIM. À BÂLE. Swiss 90,807. Comps. contg. a pyridine-3-carboxylic acid residue are treated with Et<sub>3</sub>NH. *E. g.*, the acid chloride is treated with Et<sub>3</sub>NH·HCl for two hrs. at 160°. From the product of the reaction, *pyridine-3-carboxylodiethylamide* is obtained as a yellow oil, b<sub>28</sub> 175°. It has therapeutic uses.

J. C. S.

**Aminoacetyl compounds of 4-amino-1-phenyl-2,3-dialkylpyrazolones.** FARBWERKE VORM. MEISTER, LUCIUS & BRÖNING. Austr. 86,136.—NH<sub>4</sub>OH is allowed to act on 4-chloroacetyl-amino-1-phenyl-2,3-dialkylpyrazolones, or the additive compds. of the latter with hexamethylenetetramine are treated with acids. 4-Chloroacetyl-amino-1-phenyl-2,3-dimethyl-5-pyrazolone, m. 187°, is prepd. by the action of chloroacetyl chloride on 4-amino-1-phenyl-2,3-dimethyl-5-pyrazolone. The additive compd. with hexamethylenetetramine gives by treatment with strong HCl 4-aminoacetyl-amino-

It forms a *dihydro-*

*chloride*, m. about 233°, and a *monohydrochloride*, m. 260–5°. The aminoacetyl compd. may also be prepd. by the action of NH<sub>4</sub>OH on the chloroacetyl compd. 4-Chloroacetyl-amino-1-phenyl-3-methyl-2-ethyl-5-pyrazolone (m. 186°) gives with NH<sub>4</sub>OH 4-aminoacetyl-amino-1-phenyl-3-methyl-2-ethyl-5-pyrazolone. The *hydrobromide* m. about 150°. The compds. have antipyretic properties.

J. C. S.

Water-soluble compounds of diethylbarbituric acid and its homologs. J. A. WÜLMING. Ger. 345,361. Solns. of diethylbarbituric acid or its homologs are treated with the theoretical amt. of  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ , or freshly pptd.  $\text{CaCO}_3$ , if necessary with heating, and after filtration, if required, evapd. to dryness in a vacuum. The *Ca* salt and the *Mg* salt of diethylbarbituric acid are mentioned, and also the *Ca* salt and the *Mg* salt of phenylethylbarbituric acid. The products have therapeutical uses and form stable mixts. with alk. earth salts of *o*-acetoxybenzoic acid. J. C. S.

Hydrogenated 1-alkylpyridine-3-carboxylates. RICHARD WOLFFENSTEIN. Ger. 346,888. In the place of 1-alkylhalides of alkylpyridine-3-carboxylates (C. A. 16, 2964), other quaternary  $\text{NH}_4$  salts are used. E. g., methyl 1-methylpyridine-3-carboxylate methosulfate is reduced by tin and  $\text{HCl}$  to methyl 1-methylhexahydropyridine-3-carboxylate, which is identical with the compd. obtained by reduction of the corresponding 1-alkylhalides. Ethyl 1-ethylhexahydropyridine-3-carboxylate, similarly prepd., is a basic, oily liquid. J. C. S.

Alkyl salts of hydrogenated 1-alkylpyridine-3-carboxylates. RICHARD WOLFFENSTEIN. Ger. 346,461 and 348,379; cf. C. A. 16, 2964. Hydrogenated 1-alkylpyridine-3-carboxylates are treated with alkyl halides or with other alkyl salts. By the action of  $\text{MeI}$  on methyl 1-methylhexahydropyridine-3-carboxylate in the presence of a diluent, the corresponding 1-methiodide is obtained. It is a colorless or light yellow, cryst. powder of fish-like odor, m. 185-8°. The 1-methobromide is a white, cryst. powder, m. 196°. The 1-methochloride is prepd. by the action of  $\text{HgCl}_2$  on the 1-methiodide. The ethosulfate forms white, lustrous leaflets, m. 90-6°. The ethosulfate of ethyl 1-methylhexahydropyridine-3-carboxylate is also mentioned. The products have therapeutical uses. J. C. S.

Hydrogenated 1-alkylpyridine-4-carboxylates. E. MERCK. Ger. 344,028. Trigonelline (methylbetaine of pyridine-3-carboxylic acid), its 1-alkyl homologs, or the salts of these compds. are reduced by metals in alc. soln. Reduction of trigonelline chloride by tin and  $\text{HCl}$  in  $\text{MeOH}$  soln. gives methyl 1-methylhexahydropyridine-3-carboxylate, an oil, b. 92-4°. The alkylhalides have therapeutical uses. The methiodide m. 190° (corr.). Ethyl 1-ethylhexahydropyridine-3-carboxylate, a basic-smelling, colorless oil, b. 108-10°, is obtained by reduction of ethyltrigonelline hydrochloride (? hydrobromide). The latter is prepd. by heating pyridine-3-carboxylic acid with  $\text{EtBr}$ ,  $\text{Na}_2\text{CO}_3$ , and water in a closed vessel; it forms white, lustrous spangles, m. 227° (decompn.). J. C. S.

Amino alcohols. PAUL KARRER. Ger. 347,377. Et  $\alpha$ -acetyl-amino- $\gamma$ -methyl valerate,  $\text{CHMe}_2\text{CH}_2\text{CH}(\text{NHAc})\text{CO}_2\text{Et}$ , mixed with  $\text{EtOH}$ , is allowed to act on metallic  $\text{Na}$  with occasional heating. After heating for 2 to 3 hrs. and adding  $\text{EtOH}$ , water is added and the alc. distd. off. On extrn. with ether,  $\beta$ -amino- $\delta$ -methylamyl alc.,  $\text{CHMe}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$ , is obtained as a colorless oil of basic odor, b. 194°. It forms cryst. salts with acids, e. g., the hydrosulfate or hydrochloride, m. 148-50°. An optically active (levorotatory)  $\beta$ -amino- $\delta$ -methylamyl alc. may be obtained by starting from optically active leucine.  $\beta$ -Amino- $\gamma$ -phenylpropyl alc.,  $\text{CH}_2\text{Ph}\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$ , prepd. from the  $\text{Et}$  ester of acetylphenylalanine, is a viscid oil with basic odor, b. 150-60° in a vacuum. It forms cryst. salts with acids; the hydrochloride m. 128°. By acetylation of the products of hydrolysis of casein and subsequent reduction with  $\text{Na}$  and  $\text{EtOH}$ , a mixt. of amino alcs. is obtained b.p. 50-240°. By fractionation, the following may be obtained: up to 175°/16 mm., colamine, alaninol, etc.; 105-190° [? 175-190°]/16 mm., valine alc., leucine alc., phenylalanine alc.; and a fraction distg. over at 190-235°/16 mm. The products have therapeutical uses and serve as intermediate products. J. C. S.

Carboxylic acids of the purine series. E. MERCK, OTTO WOLFFS and ERICH

KORNICK. Ger. 352,980. Salts of mono- or dialkylated xanthines are treated with salts of monohalogenated aliphatic carboxylic acids. By heating Na theobromine in aq. alk. soln. with  $\text{CH}_2\text{ClCOOH}$ , *theobromine-1-acetic acid* is obtained as colorless crystals, m.  $260^\circ$ . Theophylline and  $\text{CH}_2\text{ClCOOH}$  give *theophylline-7-acetic acid*, crystals, m.  $271^\circ$  (corr.). 3-Methylxanthineacetic acid forms needles, m.  $306^\circ$  (decompn.). Sodium 3-methylxanthine and  $\beta$ -iodopropionic acid give 3-methylxanthinepropionic acid, lustrous leaflets, m.  $308-9^\circ$  (decompn.). The *N*-alkylcarboxylic acids of mono- and dialkyl xanthines and their salts have therapeutic uses. J. C. S.

An unsaturated bile acid. J. D. RIEDEL, AKT.-GES. Ger. 352,129. Br is added to the acid prep. by an earlier pat. (C. A. 16, 3528) and the product treated with alkalies. The *diibromide* obtained by the action of Br on the  $\text{AcOH compd.}$  of *apocholic acid*,  $\text{C}_{24}\text{H}_{48}\text{O}_4\text{C}_2\text{H}_4\text{O}_2$ , is a light yellow, heavy oil. By sapon. with dil. alkali and addn. of excess of dil. HCl, an *unsatd. bile acid*, needles, m.  $245-7^\circ$ , is obtained. It is strongly antiseptic and has therapeutic uses. J. C. S.

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

The Muscle Shoals nitrate plant. Its relation to the nitrogen industry. J. K. CLEMENT. *Army Ordnance* 3, 215-8(1923); cf. C. A. 16, 2389. E. J. C.

The physico-chemical study of the lead chamber process. MAX FORRER. *Bull. soc. chim. Belg.* 31, 254-93(1922).—A detailed description of a form of app. in which  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , O, and N may be brought into contact with each other under definite conditions of pressure, temp., and, in the case of liquids, surface of reaction. The proportions of these substances could be varied at will. It is shown that, in such a system, the formation of  $\text{H}_2\text{SO}_4$  only occurs in the presence of a liquid phase, so that the system must be heterogeneous; the formation of the acid takes place in a shorter time and the yield is increased if a liquid, either  $\text{H}_2\text{SO}_4$  or  $\text{H}_2\text{O}$ , is present at the outset. Further, the rate at which water vapor is supplied during the course of the reaction exerts a considerable effect both on the velocity of reaction and on the concn. of the product. Under certain conditions, the acid formed may disappear, which appears to indicate that the reactions assumed to take place in the chambers are at least partly reversible. For low concns. of the gases, there is an optimum rate of intake for water vapor: this gives the best yield and, at the same time, the most concd. acid. As the gas concn. increases, the optimum point shifts in the direction of diminution of water supply; a curve is given showing the speed of reaction plotted against concn. of gas. The relation between these two factors is much less complex when the compn. of the liquid phase is const. F. infers from his exptl. results the existence of an intermediate substance of which water is a constituent; it is, however, decomposed in presence of an excess of water. He points out that, of the series of reactions which occur, the slowest is the "limiting reaction" in that it conditions the rate of formation of the product and shows that, in practice, the reaction velocity is strongly influenced by the rate of supply of  $\text{NO}_2$  and  $\text{H}_2\text{O}$ , but is practically unaffected by the supply of  $\text{SO}_2$ . An attempt is made to calc. the order of the reaction, and, for this purpose, the heterogeneity of the system and the non-equivalence of the reactants are neglected. The values obtained vary from 1.26 to 3.67. However, when the concn. of the liquid phase does not vary, the values are in the neighborhood of 2. In the case of temp. variations which have a similar effect to that of variations in water supply, it was not found possible to obtain a coeff. in agreement with the exptl. data. J. C. S.

The tubes used in the Claude process. I. GUILLER. *Mém. et compt. rend. travaux soc. ing. civils* 8, 320-5(1922); *Chimie et industrie* 9, 109(1923).—The com. value of the



Claude process depends to a certain extent on the life of the catalysis tubes, *i. e.*, their resistance to the combined action of high temp. ( $650^{\circ}$ ), high pressure (1,000 atm.), and the gases passing through them (especially H). The steels best suited for the work seem to be those contg. 18% W, or else nichromes. Steel contg. 13% Cr retains some of its qualities up to  $600^{\circ}$ , and A.T.G. metal (manuf. by the *Acières d'Imphy*) presents the greatest mech. strength at high temps. and the greatest resistance to the action of  $\text{NH}_3$ . G. examd. 2 tubes used by Claude. The first was used in the first trials at 1,000 atm., and was attacked by H at  $550^{\circ}$  after operating for 60 hrs.; microscopic examn. showed that a filament had formed where ferrite preëxisted, but there did not seem to be decarburization. The 2nd tube was made of B.T.G. metal from the *Acières d'Imphy*, and had burst after being in use for 3,300 hrs.; owing to flooding there was no decarburization. The presence of Cr and W seems to give a resistant carbide. At any rate it would be easy to make a C-free alloy by using Mond Ni, electrolytic Ni, aluminothermic Cr or specially refined Cr.

A. P.-C.

**The Claude process for the manufacture of ammonia.** M. LHEURE. *Mém. et compt. rend. travaux soc. ing. civils* 8, 326-33(1922); *Chimie et industrie* 9, 109(1923).—A comparison, from an economic standpoint, of the Claude and Haber processes. Neglecting the increased life of tubes, utilization of the vapors produced by cooling of the gases after each stage of catalysis, and the utilization of the "frigories" in the anhyd.  $\text{NH}_3$ , which are all in favor of the Claude process, M. concludes that the cost of fixing N by the Claude process is 18% lower than by the Haber process.

A. P.-C.

**The presence of acetone in the ammonia of commerce.** J. BOUGAULT AND R. GROS. *J. pharm. chim.* 26, 381(1922); cf. *C. A.* 16, 4301.—The priority of Labat's observation (*C. A.* 4, 234) is admitted.

S. W.

**The (French) nitrogen policy.** FERDINAND GROS. *Mém. et compt. rend. travaux soc. ing. civils* 8, 172-203(1922); *Chimie et industrie* 9, 108(1923).—A discussion of French requirement of nitric N, from which G. concludes that the most economic synthetic process (for France) is the arc process, and then the cyanamide process.

A. P.-C.

**The Harber process.** M. PATARY. *Mém. et compt. rend. travaux soc. ing. civils* 8, 203-35(1922); *Chimie et industrie* 9, 108(1923).—A comparison of the Haber and competing processes from an economical standpoint, showing its advantages.

A. P.-C.

**The manufacture of cyanamide.** GARAIX. *Mém. et compt. rend. travaux soc. ing. civils* 8, 290-2(1922); *Chimie et industrie* 9, 108(1923); cf. *C. A.* 16, 4301.—G. outlines the development of the manuf. of cyanamide, and then discusses its cost of production, comparing it with the Haber process and showing its economic advantages over the latter. At the Martigny plant of the Société des Produits Azotés it is converted into urea as follows: A suspension of cyanamide in water is treated with  $\text{CO}_2$  (from the  $\text{CaO}$  kilns of the  $\text{CaC}_2$  plant), filtered to remove  $\text{CaCO}_3$ , and when the concn. of  $\text{CN}_2\text{H}_2$  has reached the desired point  $\text{H}_2\text{SO}_4$  is added to catalyze hydration ( $\text{CN}_2\text{H}_2 + \text{H}_2\text{O} = \text{CO}(\text{NH}_2)_2$ ). The soln. is then treated with natural  $\text{Ca}_3\text{P}_2\text{O}_8$ , which gives a fertilizer contg. sol.  $\text{P}_2\text{O}_5$  and  $\text{CO}(\text{NH}_2)_2$ , known commercially as "phosphazote."

A. P.-C.

**The manufacture of sulfate of ammonia.** A. GREBEL. *Chimie et industrie* 9, 26-42(1923).—A detailed analysis of manuf. with suggested improvements for modern French practice.

A. P.-C.

**Note on stabilized bleaching powder for tropical use.** F. S. AUMONIER AND S. ELLIOTT. *J. Royal Army Med. Corps* 39, 459-60(1922); *Pub. Health Eng. Absts.* Feb. 24, 1923.—Bleach stabilized with 20%  $\text{CaO}$  stands storage on a lab. scale in tropical climates and does not deteriorate to any appreciable extent for a few days after opening. Stoneware jars had no advantages over sealed tins. On a large scale the mixt. tended to "fire" and lose Cl, but the difficulty was minimized by the control of the temp. (temps. used are not stated).

G. C. BAKER

**Fluorspar.** Its uses in steel manufacture and other industries. G. H. JONES. *Raw Material* 6, 58-63(1923); cf. C. A. 17, 452.—A general article. E. J. C.

**Barytes:** Occurrence, mining, uses. R. B. LADOO. *Eng. Mining J.-Press* 115, 319-24(1923). E. J. C.

**Mining and washing phosphate rock in Tennessee.** R. W. SMITH. *Eng. Mining J.-Press* 115, 221-6(1923). E. J. C.

**Sulfur and pyrites in 1921.** H. A. C. JENISON AND H. M. MEYER. U. S. Geol. Survey, *Mineral Resources of U. S., 1921*, Pt. II, 169-73 (Preprint No. 26, publ. Dec. 29, 1922). E. J. C.

**The monazite industry in its relation to rare earths and radioactivity.** EDMUND WHITE. *Pharm. J.* 109, 440-2; *Chemist and Druggist* 97, 671-2(1922).—An illustrated address on monazite, the methods of obtaining it and its treatment for *ext. of Th* and *meso-Th* at Travancore, India. S. WALDBOTT

**The future supply of carbon black.** R. L. CARR. *India Rubber Rev.* 22, No. 12, 20, 23, 134(1922).—A description of the economic and legal status of the present industry, its extent and its prospects. C. C. DAVIS

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#### Explosions in liquid air plants, 24.

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**Phosphoric acid.** A. KELLY. Can. 228,247, Jan. 23, 1923. Mineral phosphates are roasted to carbonize the org. matter, the latter is then removed by oxidation and the roasted phosphate treated with an acid to produce  $H_3PO_4$ . Cf. C. A. 16, 3734.

**Hydrocyanic acid.** F. J. METZGER. Can. 228,392, Jan. 30, 1923. Crude solid products contg. cyanides are subjected to the action of  $CO_2$  and the temp. of the mass is regulated so as to prevent the polymerization of the HCN.

**Hydrocyanic acid.** F. J. METZGER. Can. 228,393, Jan. 30, 1923. HCN is recovered from cyanide-contg. material by causing  $CO_2$ , 1.5-3 times the theoretical quantity required, to pass through the material in 6-12 min.

**Purifying liquid hydrocyanic acid.** M. J. BROWN. U. S. 1,444,300, Feb. 6. "Commercial" liquid HCN is heated to within about  $10^\circ$  of its b. p. to drive off  $CO_2$  or other gaseous impurities without any substantial vaporization of the HCN.

**Furnace tubes.** F. J. METZGER. Can. 228,239, Jan. 23, 1923. A furnace tube suitable for use in heating alkali metal compds. and C in the presence of N has a thin inner shell of ferrous metal and an outer shell of nichrome, the walls of the shells being spaced and a conducting filler disposed between the walls.

**Recovery of zinc as basic sulfate.** E. P. STEVENSON. U. S. 1,444,484, Feb. 6. Material contg. Zn in the form of an oxide, carbonate or hydroxide is treated with a concd. soln. of  $(NH_4)_2SO_4$  at a temp. of about  $100^\circ$  to dissolve out the Zn, and the soln. is cooled to ppt. out a basic sulfate of Zn.

**Barium carbonate.** J. H. MACMAHON. U. S. 1,444,623, Feb. 6.  $BaCO_3$  is prepd. by reaction between BaS and the  $(NH_4)_2CO_3$  in the liquor coming from the bicarbonate filters of the "ammonia soda" process.

**Sodium dekaborate.** W. VOSS. U. S. 1,444,989, Feb. 13. Boronatrocalcite is combined with just sufficient dil.  $H_3BO_3$  and  $H_2SO_4$  soln. to form Na dekaborate and is heated to about  $75^\circ$ .

**Anhydrous chlorides from free metals.** B. H. JACOBSON. U. S. 1,445,082, Feb. 13. Al, Sn, Sb, As or other free metal is treated with Br and Cl to form the chloride.

**Treating silicates with acids.** G. A. BLANC. U. S. 1,443,674, Jan. 30. In treating silicates, e. g., leucite, with acids to obtain saline solns. free from silica, the acid liquid is repeatedly passed through a layer of granulated silicate and after each passage through

the layer is enriched with the dissolved salts and reduced in acidity. This operation is continued to obtain as complete a reaction as possible with retention of the colloidal silica in the layer of insol. residue.

**Solidifying silicate detergents or similar materials.** E. COWLES. U. S. 1,445,004, Feb. 13. A detergent formed of Al and Na silicates and NaOH (cf. U. S. 1,419,625, C. A. 16, 2761) or other material which solidifies at a temp. higher than that which causes a viscous condition is spread on a cooling drum in viscous condition and after some cooling but while still largely in viscous condition is scraped off the drum and allowed to fall on to a traveling belt on which it solidifies with evolution of heat and elevation of temp. while exposed to the air.

**Isolation of alumina from clay.** HIROSHI TANAKA and the TOKYO KÔGYÔ SHIKENJO. Japan. 40,177, Oct. 3, 1921. Powdered clay is burned to a porous mass, mixed with concd.  $\text{H}_2\text{SO}_4$  at low temp. and the mixt. is heated in a Pb-lined autoclave with agitation. When the reaction is completed the mixt. is cooled and filtered in the absence of air. The filtrate is heated at  $100^\circ$  in the absence of air to decompose  $\text{Al}_2(\text{SO}_4)_3$  into  $\text{Al}_2\text{O}_3$  and  $\text{SO}_2$ . A product of high purity is obtained.

**Precipitating iron in aluminous solutions.** T. MEJDELL. U. S. 1,444,160, Feb. 6. Acid aluminous solns. contg. trivalent Fe are partly neutralized by hydrolysis of the Al salt and by adding an Fe compd. from a previous pptn. as catalyzer. The Fe compd. used is activated by treating it with Fe oxide or fresh raw material contg. Fe and Al.

**Recovering nitrogen oxide vapors.** P. A. GUYE and A. SCHMIDT. U. S. 1,443,220, Jan. 23. N oxides mixed with other gases such as result from partial reaction of N and O are recovered by condensing them with anhyd.  $\text{Al}_2\text{O}_3$  obtained by dehydrating hydrous alumina at temps. of not over  $400^\circ$ . Temps. of  $-20^\circ$  to  $-80^\circ$  are preferably used for the condensation.

**Apparatus for fixation of atmospheric nitrogen.** TEITARÔ MITSUDA and YASUJIRÔ TAMBA. Japan. 40,056, Sept. 21, 1921. Addn. to 32,722. At the same time that an arc of high potential is produced a static elec. field of high intensity is produced in a contacting surface of the arc and air; the large quantity of air thus ionized facilitates the formation of N oxides.

**Apparatus for collecting potassium.** W. T. SYMONS. Can. 228,379, Jan. 30, 1923. A horizontal flue has spaced openings in its side; in these are placed easily removable filter members over which water is sprayed.

**Carbohydrate ethers as protective colloids.** L. LILIENFELD. U. S. 1,444,257, Feb. 6. Methylcellulose, ethyl or methyl starch ethers, or  $\text{H}_2\text{O}$ -sol. ethylcellulose and similar carbohydrate ethers are used as protective colloids in the prepn. of colloidal medicinal or other products, or for prepg. emulsions or salve-like compns. contg. phenols. Numerous examples are given of methods of prepg. these compns.

**Pitch emulsions, briquet binders, electrodes, artificial charcoal, etc.** J. C. MORRELL. U. S. 1,440,355, Dec. 26. A light colored soln. formed from tannic acid and  $\text{NH}_4\text{OH}$  is used to produce a suspension of hard pitch and an emulsion of heavy coal-tar oil which may be used together as binders with fuel briquet materials in which the pitch and oil are proportioned as desired or may be used for prepg. electrode mixts. or absorbing charcoal. C black, fuller's earth and the like will completely adsorb the pitch and oil from the emulsions. Compns. of this kind are also suitable for use as road binders or to lay dust. U. S. 1,440,356 relates to similar prepn. contg. asphaltic and oleaginous materials dispersed in a protective colloidal medium.

**Bleaching-powder solutions.** J. H. MACMAHON. Can. 228,060, Jan. 16, 1923. A bleaching powder of stable character, substantially free from excess lime and from any

markedly alk. reaction is prepd. by mixing bleaching powder contg. an excess of lime with water and treating the mixt. with Cl.

**Transparent sheets of gelatin composition.** K. L. WEBER. U. S. 1,442,917, Jan. 23. Sheets which are waterproof and may be used for windowpanes are prepd. from a gelatin and glycerol compn. They are coated with transparent, waterproof varnish.

**Fire-proofing composition.** C. R. ALLISON. U. S. 1,444,051, Feb. 6. A compn. adapted for rendering wood or other materials fire-resistant is prepd. by making a paste of "Zn-skimmings" (obtained from galvanizing baths as a dross) and  $H_2O$ , allowing the paste to "age" for several days and then mixing it with linseed oil, fish oil, tar oil or a similar vehicle, white lead,  $NH_4Cl$  and turpentine.

**Polishing composition.** W. H. PHELPS. U. S. 1,445,034, Feb. 13. A polish for use on furniture or leather is formed of kerosene 9 pints, straw paraffin oil 40 pints, oil of mirbane 1 lb., and alkanet root 1 lb.

**Smoke production.** J. H. HAMMOND, JR. and H. L. F. BUSWELL. U. S. 1,444,312, Feb. 6. A gasoline flame is directed upon combustible material and a combustion retarder (e. g., pitch and  $CaCO_3$ ) in a closed chamber, with a restricted air supply. The smoke is led off through an exit pipe.

**Lime kiln.** V. ARNOLD. U. S. 1,442,845, Jan. 23. The walls of the kiln are undulated, which serves to regulate the flow of material through the kiln.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**Coloring glass with nickel.** KITSUZO FUHA. *J. Japan. Ceram. Assoc.* **361**, 414 (1922).—Numerous batches were melted to find the coloring action of Ni and its compds. on various glasses with or without the addn. of oxidizing or reducing agents. Conclusions: (1)  $NiO$  gives purple with K glasses and dark brown with Na glasses, though these effects become less distinct as the amt. of  $NiO$  increases. (2) The difference in the bivalent metal of a glass formula does not affect the color materially except Ba which has a peculiar effect on the color produced by  $NiO$ . (3) In borosilicate glasses,  $NiO$  produces pinkish purple. (4) Metallic Ni or  $NiCO_3$  may be used instead of  $NiO$ . (5) The presence of an oxidizing agent ( $KNO_3$ ), reducing agent (K tartrate) or  $As_2O_3$  in batches does not affect the color given by  $NiO$ . S. KONDO

**Feldspar for glassmakers.** F. C. FLINT. *J. Am. Ceram. Soc.* **6**, 413-6 (1923).—A coarser grinding than for pottery use is desirable for the sake of economy and freedom from Fe contamination. Alkali,  $Al_2O_3$  and  $Fe_2O_3$  contents must be const. C. H. K.

**Report of the work of the ceramic division.** JOSEPH KEEBLE. Can. Dept. Mines, *Summary Report No. 574*, 55-71 (1922).—The Canadian deposits of brick, fire, pottery and special clays are described. L. W. RIGGS

**The meaning and microscopic measurement of average particle size.** G. ST. J. PERROTT AND S. P. KINNEY. *J. Am. Ceram. Soc.* **6**, 417-39 (1923).—The value for effective av. particle size suggested for use in dealing with ceramic materials is  $d_{av} = y_d/100 = 2nd^2/2nd^2$ , where  $y_s$  is the % of total surface represented by particles of diam.  $d$ , and  $n$  is the relative number of particles of diam.  $d$ . C. H. KERR

**Some notes on historical and modern (ceramic) decorative processes.** F. H. RHEAD. *J. Am. Ceram. Soc.* **6**, 356-97 (1923). C. H. KERR

**Scientific aspects of China's ancient pottery industry.** G. WANG. *Science (China)* **6**, 869-82 (1921).—The manuf. of glazed ware in China dates from about the year 100

B.C. The excellence of the early pottery ware was due to the use by the Chinese of a feldspar glaze and high temps. Cu, Fe and Pb colors were largely used. There is no evidence of the use of Cr or U compds. A type of furnace built on the principle of the Hoffman Ring Furnace has been in use for at least 1000 years. WM. H. ADOLPH

**Impact tests on tableware.** H. H. SORTWELL. *J. Am. Ceram. Soc.* **6**, 349-55 (1923).—Five potteries, 3 making semi-porcelain and 2 vitrified china, submitted 7-in. plates for test. The plates were struck in the center. Both "starring" and complete failure were observed. In all types the impact to cause "starring" increased with thickness in an approx. parabolic relation, but complete failure was almost independent of thickness (between  $\frac{1}{8}$  and  $\frac{3}{8}$  in.) except in double-thick semi-porcelain with heavy rim reinforcing. C. H. KERR

**Report on the Manchurian magnesite.** KOSUKE HIRANO. *J. Japan. Ceram. Assoc.* **361**, 414-23(1922).—Color, appearance, sp. gr., chem. compn. and burning behaviors of 102 specimens of magnesites which were collected from all mine lots possessed by the South Manchurian R. R. Co. except the Mt. Kamba and the Mt. Gyushin (whose magnesites were reported by H. in April 1919) are described in detail. The range of sp. gr. is 2.76-3.01. They have the following compns.: 0.20-30.28  $\text{SiO}_2$ , 0-1.80  $\text{Al}_2\text{O}_3$ , 0.18-4.37  $\text{Fe}_2\text{O}_3$ , 0-24.12 CaO, 16.32-47.02 MgO and 36.20-51.78% loss on ignition. S. KONDO

**Brick.** T. R. LAWSON, *et al.* *Proc. Am. Soc. Testing Materials* **22**, I, 248-9 (1922).—The new tentative standard reduces the number of sizes and types of paving brick from 66 to 7. R. T. MONTGOMERY

**Clay and cement sewer pipe.** R. HERING, *et al.* *Proc. Am. Soc. Testing Materials* **22**, I, 252-3(1922).—New tentative standard calls for a test of not less than 5 pieces. Av. crushing strength (lbs. per linear ft.) is from 1,000 for 4" internal diam. to 3520 for 42" pipe, knife edge or 3 point bearings being used. For sand bearing the av. is 1430 lbs. for 4" pipe to 5030 for 42" pipe. Max. absorption is 8%. A rejected shipment may be culled and retested. R. J. MONTGOMERY

**Fireproofing.** I. H. WOOLSON, *et al.* *Proc. Am. Soc. Testing Materials* **22**, I, 254-8(1922).—New tentative standard includes 5 new sections on size of sample, loading, measurements, position of nozzle and conditions of acceptance. R. J. M.

**Drain tile.** A. MARSTON, *et al.* *Proc. Am. Soc. Testing Materials* **22**, I, 259-63 (1922).—No changes are made in standard specifications. Progress is being made on tests of the effect of acids and alkalis in the soil. R. J. MONTGOMERY

**Report of committee on precision and tolerances.** R. C. PURDY, *et al.* *Proc. Am. Soc. Testing Materials* **22**, I, 316-20(1922).—Errors in testing refractory materials under load at high temps. may be due to (a) inaccurate temp. control ( $10^\circ$ ), (b) incorrect pressure (0.6 to 0.9%), (c) eccentric loading (may be several hundred %), (d) errors in detg. length of brick (0.03 in.). Probable error in results is 5 to 10% of reported deformation. The softening point of a fire brick can be checked within  $\frac{1}{2}$  cone. Exterior vol. of a test piece can be checked within 5%; apparent sp. gr. to 0.01; true sp. gr. to 0.02; vol. of open pores to 0.5%; sealed pores to 0.8 cc. for a standard sample of about 128 cc. vol.; and shrinkage to 0.25 cc. for a 128 cc. sample. Modulus of rupture tests on  $\text{SiO}_2$  brick will check within 3% if 15 bricks are averaged for a test. The error in measurement of brick dimensions is 0.2% in length, 0.4% in breadth and 1.2% in thickness. R. J. MONTGOMERY

**Italian talc and graphite.** Two Alpine quality products. CHAS. MATHIEU. *Raw Material* **6**, 67-8(1923). E. J. C.

**How to install and operate a fuel oil system.** J. D. LALOR. *J. Am. Ceram. Soc.* **6**, 448-61(1923). C. H. KERR

Fuel oil as applied to periodic up-draft kilns in the manufacture of high-tension electrical porcelain. L. H. BROWN. *J. Am. Ceram. Soc.* 6, 462-5(1923).

C. H. KERR

Manufacture of spark plug porcelain. A. G. WIKOFF. *Chem. Met. Eng.* 28, 150-7(1923).—The plant of the Champion Porcelain Co. of Detroit is described. The body approaches sillimanite in compn. Details of manuf. are given. R. J. M.

The problem of turquoise alkaline glaze. M. M. FRENCH. *J. Am. Ceram. Soc.* 6, 405-8(1923).—A suitable body must have 60-64% free flint. Adding 4-8% kryolite will lower the firing temp. The sum of the ball clay (J. P. No. 9), Georgia clay and feldspar may vary 28-34%. With Cornwall stone the body appears more like porcelain. A little whiting may be added, if desired. The glaze was 0.6 Na<sub>2</sub>O, 0.1 K<sub>2</sub>O, 0.3 CaO, 2.8 SiO<sub>2</sub>. With 0.7 Na<sub>2</sub>O and 0.3 CaO the results were equally good. Com. application is doubtful because of the great amt. of attention required. C. H. KERR

The artistic needs of modern faience. C. DRESSLER. *J. Am. Ceram. Soc.* 6, 398-404(1923).

C. H. KERR

The polarizing microscope as an aid in feldspar standardization. H. C. ARNOLD. *J. Am. Ceram. Soc.* 6, 409-12(1923).

C. H. KERR

A study of the slag test (for refractories). R. M. HOWE. *J. Am. Ceram. Soc.* 6, 466-73(1923).—Many data on the penetration method of slagging testing showed little or no relation between lab. tests and factory results. A newer method based upon the depression of the m. p. of ground samples of the refractories by addns. of known slags appears to give more reliable information than the old penetration tests. Further work is under way. C. H. KERR

C. H. KERR

Technical electroösmosis (PRAUSNITZ) 4. Porcelain clays of Ballerat (CALLISTER)

8.

Glass composition. W. C. TAYLOR. *Can.* 227,457, Dec. 26, 1922. A glass contains over 70% SiO<sub>2</sub>, over 2% B<sub>2</sub>O<sub>3</sub> and a halogen compd.

Furnace for molten glass. C. S. STAFFORD. U. S. 1,443,767, Jan. 30. The walls of the furnace are formed of blocks or slabs of refractory material the outer faces of which are treated with waterproofing material, e. g., brass, cement or enamel, so that cooling liquid can be applied directly to them without damage.

Continuous cooling furnace for glass vessels. TAMESABURÖ YAMAMOTO. *Japan.* 40,047, Sept. 20, 1921.

Glass-melting furnace. SADAJIRÖ KÖNO. *Japan.* 40,098, 40,099, and 40,100 (additions to 35,150). Sept. 28, 1921. Diagrammatical descriptions.

Bonding carbide grains with ceramic material. M. F. BRECHER and M. C. BOOZE. U. S. 1,444,162, Feb. 6. Grains of Si carbide or similar material are mixed with a ceramic binder such as a plastic clay compn. and the mixt. is fired in the presence of reducing gases or other medium which will prevent oxidation.

"Safety-tread" ceramic tile. G. N. JEPSON and M. F. BRECHER. U. S. 1,445,083, Feb. 13. Vitrified tiles of ceramic material are formed with cryst. granules of Al<sub>2</sub>O<sub>3</sub> or other abrasive material integrally embedded within the superficial or tread portion of the tile.

Refractory material for furnaces. C. A. SCHARSCHU. U. S. 1,444,527, Feb. 6. A refractory compn. is formed in part of a coherent mixt. of crystd. MgO, calcined MgO of lower d. and C and in part of a subvitreous monolithic layer of MgO particles bound together by sublimed MgO. This layer has a mass d. of 3.5-3.6 and is so hard that it has a metallic ring even at elec. furnace temps. and it undergoes no material expansion or contraction at temps. up to 1800°.

**Abrasive composition.** H. M. OLSON. U. S. 1,444,479, Feb. 6. A hard cryst. abrasive compn. is formed from non-cryst.  $\text{SiO}_2$  88, alum 2 and lime 10%, collectively treated with  $\text{H}_2\text{O}$  and calcined.

**Enamel.** A. L. D. D'ADRIAN. U. S. 1,443,813, Jan. 30. Lepidolite is fused with an enamel frit to produce an enamel adapted for use on cooking vessels.

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

**Cement in 1921.** BELLE W. BAGLEY. U. S. Geol. Survey, *Mineral Resources of U. S., 1921*, Pt. II, 215-28(preprint No. 28, publ. Jan. 8, 1923). E. J. C.

**Stone in 1921.** G. F. LOUGHLIN AND A. T. COONS. U. S. Geol. Survey, *Mineral Resources of U. S., 1921*, Pt. II, 175-213(preprint No. 27, publ. Jan. 22, 1923). E. J. C.

**Setting and velocity of solution of burnt gypsum.** P. P. BUDNIKOV AND JA., K. SYRKIN. *Bull. Inst. Polyt. Ivanovo-Voznesensk.* 6, 235-47(1922).—The authors have investigated the velocities of dissolution of gypsum after the latter had been heated at various temps., the concns. being detd. at different stages of the dissolution by means of cond. measurements. For the samples which have been heated at 115° and 125°, the cond. and hence the soly. increases rapidly to a point corresponding with a soln. considerably supersatd. with respect to  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ , and afterwards diminishes, at first rapidly and then slowly, but still indicates a certain degree of supersatn. after 24 hrs. Supersatd. solns. are obtained also with gypsum heated at 400°, but not when a temp. of 500° is reached. In so far as the setting of gypsum is conditioned by crystn. from supersatd. solns., the temp. at which "dead-burnt" gypsum is formed may therefore be assumed to be about 450°. Burnt gypsum may be regarded as consisting of two components, one sol., which dissolves readily, and the other relatively insol. The soly. of samples which have been burnt at temps. between 500° and 800° is rapid at first, this being explained by the presence of appreciable proportions of the sol. modification in dead-burnt gypsum. The time occupied by dissolution does not furnish an exhaustive explanation of the disappearance of the ability of gypsum to set, and the authors suggest that the presence of the insol. component in the interstices of the crystals prevents the latter from growing.

J. C. S.

**Effect of chemical solutions on various woods used in tanks.** S. J. HAUSER AND CLARENCE BAHLMAN. *Chem. Met. Eng.* 28, 159-63(1923).—Uniform test strips of air-seasoned red gulf cypress, Douglas fir, long-leaf yellow pine, California redwood, hard maple, and white oak were treated with hot and cold solns. of common acids, alkalies, and salts, as well as linseed oil, turpentine, and the fatty acids of cottonseed oil. Absorption of the liquids, expansion or contraction of wood, and other physical changes were noted. Relative amts. of color and taste imparted to water by the woods were recorded. Cypress imparts neither appreciable color nor taste to water. Redwood and oak yield colored aq. solns. Fir and pine give aq. solns. with pronounced tastes. While all woods absorb the various solns. or chemical to a certain degree, oak, maple, and redwood have the greatest absorptive powers. In general the woods absorb the chemicals in the following descending order, NaOH and other alkaline solns., acids, common salts, org. liquids. NaOH, HCl,  $\text{HNO}_3$  and bleaching powder and hot org. liquids tend to shrink the woods. This effect is greatest with oak and maple and least pronounced with pine and cypress. The most corrosive solns. tested were  $\text{HNO}_3$  and NaOH, followed by  $\text{H}_2\text{SO}_4$ , HCl and bleaching powder. Other solns. had little corrosive action. Of 38 liquids or solns. tested the number which appreciably affected the differ-

ent woods at room temp. are as follows: redwood 22, oak 15, maple 13, fir 8, cypress 7, and pine 4.

LOUIS E. WISE

**Wood decay.** III. **Toxicity of western yellow pine crude oil to *Lenzites saepiaria* Fries.** HENRY SCHMITZ. *J. Ind. Eng. Chem.* **14**, 617-8(1922).—Crude oil obtained by distg. western yellow pine evaps. so rapidly and is so slightly toxic that it has little value as a general wood preservative. It may possibly be adapted to special uses as in shingle stain and preservative paint mfg. S. detd. the toxic concn. using sawdust from white fir (*Abies grandis*), Douglas fir (*Pseudotsuga taxifolia*), and sugar maple (*Acer saccharum*) as culture media, and noting the lowest concn. of oil at which fungal growth was prevented. The toxic concns. are 9-10% for white fir, 10-11% for Douglas fir, and 11-12% for hard maple. S. suggests a method of detg. toxicity of wood preservatives towards fungi.

L. E. WISE

Modern research on anti-fouling paints and a note on wood borers (GARDNER) 26.

• **Cement mixture.** F. FERRARI. U. S. 1,444,309, Feb. 6. A cement mixt. (adapted for withstanding sea water or water containing sulfates) is prepd. by grinding pozzuolanic substances and a special cement contg.  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  free of aluminates and ferrites of Ca, proportioned according to the amts. of available CaO and sand in practical use.

**Elastic cement.** W. T. GODDARD. Can. 227,950, Jan. 16, 1923. A cement contains a non-friable aggregate, part of which is initially coated with rubber. Cf. C. A. **16**, 1642.

**Elastic cement.** RISSYO TAKAHASHI. Japan. 40,020, Sept. 10, 1921. Thirty parts of soln. of  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{BaCl}_2$  of 12° Bé. is gradually added to a mixt. of  $\text{BaSO}_4$ , 100 and Turkey red oil 30 and thoroughly mixed together; the insol. elastic substance sepd. from them is completely washed with  $\text{H}_2\text{O}$  and dried *in vacuo*. It is then used for replenishment or manuf. of plastic materials.

**Waterproof tile.** MANZÔ SUGIZAKI. Japan. 40,080, Sept. 28, 1921. Tile prepd. from mortar or cement is heated to about 120°, painted with Japanese lac and then covered with Cu powder. It is once more heated at about 120°. It is resistant to heat and  $\text{H}_2\text{O}$ .

**Building material.** P. E. SINNETT. U. S. 1,443,097, Jan. 23. Building blocks are formed of sawdust, ground wood or other fibrous material,  $\text{MgO}$  and  $\text{MgCl}_2$ .

**Antiseptic for wood.** KIVOSHI MATSUI. Japan. 40,024, Sept. 20, 1921. Soy-bean oil (2.010 g.) is saponified by boiling with 20% NaOH soln.;  $\text{CuSO}_4$  (1.005 g.) in warm  $\text{H}_2\text{O}$  is added; and the product is warmed and sepd. from  $\text{H}_2\text{O}$ . It is then mixed with petroleum (181) of 24-28° Bé., naphtha (562.5 g.), and  $\text{C}_6\text{H}_5\text{OH}$  (187.5 g.) and agitated at about 80°. It has light color and drastic action.

**Preservative for wood posts or piles.** M. G. WEBER. U. S. 1,443,602, Jan. 30. Creosote 300, an As or Zn salt or Cu stearate or resinate 15-30, dinitrobenzene 7-10, dinitrochlorobenzene 7-10 and *p*-dichlorobenzene 7-10 parts.

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

**Economic combustion of waste fuels.** D. M. MEYERS. *Bur. Mincs. Tech. Paper* **279**, 51 pp.(1922).—Waste fuels are classified as "autocombustibles" and "semicom-bustibles." Methods are discussed for obtaining: (1) high temp., (2) correct amt. of air supply and (3) complete mixt. of the air with the fuel gas when waste materials are



used as fuels. Twenty illustrations show the variations in furnace design which have proved valuable in utilizing as fuels sawdust and wood waste, tan bark, chestnut ext. chips, paper-mill wastes, bagasse and city refuse. The construction and relative advantages of these furnaces are discussed. Licorice chips and coke breeze as fuels are briefly treated. Methods are given for calcg. the *calorific value* of this class of fuels. Dulong's and similar formulas give inaccurate results when applied to waste fuels, especially those high in O. Data obtained in a number of steam tests with the above waste as fuels are included in the paper. As each waste material has its own peculiar physical and chem. characteristics so each presents a special problem in combustion and furnace design in order to effect its efficient utilization for fuel purposes. Past investigations along these lines have resulted in great savings in fuel costs. W. W. HODGE

The use of Limburg waste fuels for power. A. J. TER LINDEN. *De Ingenieur* 37, 282-97(1922); *Fuel Economy Rev.* 2, No. 2(Aug. 1922).—New methods are described for efficiently utilizing refuse from collieries. The difficulty of using such fuels can only be overcome by obtaining a much more efficient ash-removal device coupled with a grate design which will allow a more complete combustion. R. BEUTNER

Judging the combustion of liquid fuels. A. G. WITTING. *Blast Furnace Steel Plant* 11, 125-7(1923); cf. *C. A.* 16, 3749.—A formula is developed for calcg. the results of combustion from the waste-gas analysis applied to liquid fuels. J. L. WILEY

Gas producers and producer gas. VICTOR WINDETT. *Blast Furnace Steel Plant* 11, 55-60(1923).—A discussion of what constitutes correct practice. J. L. WILEY

The determination of volatile matter in fuels. P. WEDGWOOD AND H. J. HODSMAN. *J. Soc. Chem. Ind.* 41, 372-4T(1922).—Monel metal and calorized steel crucibles were studied as substitutes for Pt in the Am. Chem. Soc. method for volatile matter. The dimensions were those of the Pt crucible. The results are consistent, but about 0.5% lower than with Pt, owing to oxidation of the crucible, less loss by entrainment, and the fact that 3 min. instead of 1 min. are required to reach 930°. Monel metal is the better; it was still good after 50 detns. ERNEST W. THIELE

Mechanical installations for the complete utilization of fuels containing tar. ERNEST BLAU. *Chem.-Ztg.* 46, 1121-2(1922).—A description in general terms, not illustrated, of low-temp. carbonization app., especially for the recovery of tars. They are: a rotating internally fired kiln, 2 producers, and a distn. retort attached directly to a boiler furnace. ERNEST W. THIELE

The national carburettants and their scientific study. DANIEL BERTHELOT. *Rev. sci.* Dec. 9th, 1922.—A review of the present French situation as regards the use of liquid fuels, especially alc. C. H. HERTY, JR.

Low-temperature carbonization. II. Low-temperature products. HARALD NIELSEN. *Beama* 12, 28-36(1923).—Coals are blended to produce low-temp. coke approaching blast-furnace cokes in hardness and strength. Photos are given showing textures of coke produced under different conditions. The carbonization process is developed in steps. N. claims that the lower the temp. the greater the probability of obtaining a high yield of paraffinoid bodies. Internal heating avoids cracking of low-temp. oils by contact with highly heated walls, as in externally heated retorts. The % of light fraction in the tar up to 170° is less in internal heating. Different oil fractions and quantities produced are given. The formation and decompn. of CH<sub>4</sub> with regard to temp. and gas-vol. conditions are discussed in detail. N. considers the various conditions affecting the formation of NH<sub>3</sub> and contends that internal heating tends to increase its yield. Cf. *C. A.* 16, 2209. A. H. DICK

The low-temperature carbonization of coal. I. The development of the carbocoal process at the Irvington plant of the International Coal Products Corporation. H. A.

CURTIS AND W. J. CHAPMAN. *Chem. Met. Eng.* 28, 11-7(1923).—A detailed description with cuts of 8 large-scale exptl. retorts, concluding with a summary of the information gained by 6 yrs.' experimentation with them. (Cf. *C. A.* 12, 1594; 14, 2850, 3519; 15, 1799.) II. Results of applying the carbocoal process to various types of coal in small-scale apparatus. H. A. CURTIS AND W. J. GELDARD. *Ibid* 60-2.—Description with cuts of small-scale app. and of exptl. procedure. Data on runs for high-volatile bituminous, Texas lignite, medium-volatile, high-ash bituminous and 16 miscellaneous coals. The relation between these small-scale results and large-scale results is not given. III. The Clinchfield carbocoal plant. H. A. CURTIS AND E. E. DAUCHRON. *Ibid* 118-23.—The plant consisted of 24 primary retorts, a grinding, fluxing and briquetting plant and 30 secondary retorts. While based upon the Irvington experience, in many points this was disregarded. Operating difficulties and remedies are given as follows: 1.—Breakage of stirrers from carbon deposits. This was remedied by making the paddles with light steel tips which yielded first. 2.—The "Vesuvius" discharger was replaced by an inclined cooling chamber with a water sealed door. 3.—Belt conveyors for the hot semi-coke gave way to hopper cars but a bucket conveyor would probably work. 4.—Clogging of gas off-take of primary retort was alleviated by liquor sprays. 5.—Grinding the semi-coke with ball mills gave high power cost. Smaller rod mills might be better. 6.—The wear on chains in the briquet press is excessive. A Belgian press without chains is suggested. 7.—Storing raw briquets in deep bins and feeding roughly by gravity gave poor results. The raw briquet must be handled with care. 8.—Inclined chambers for secondary retorts gave uneven heating and the briquets stuck. This trouble was not solved. In spite of difficulties the plant operated and marketed the product, but costs were too high. IV. Improved type of primary retort for low-temperature carbonation and results obtained therewith. H. A. CURTIS AND W. J. GELDARD. *Ibid* 171-3.—Describes a retort used at Irvington which was a modification of the Clinchfield retort in 4 main points. (1) A removable cast iron top on the retort instead of a complete carborundum muffle. This was cheaper and greatly facilitated cleaning the carbon deposit from the retort. (2) Regenerative heating instead of recuperation gave cheaper construction and better heat control. (3) Placing the discharge screws right below the floor of the retort in place of at the bottom of a chute lessened discharge troubles. (4) Increased agitation with more paddles and greater shaft speed increased the capacity of the retort. Operating data show that this retort is a distinct advance though not the last word in low-temp. carbonization. J. J. MORGAN

Coal. A. C. FIELDNER, et al. *Proc. Am. Soc. Testing Materials* 22, I, 459-62 (1922).—Report of Comm. D-5. The micropyrometer method for coal ash fusibility (*C. A.* 16, 3381) was compared with the standard gas-furnace method (*C. A.* 14, 1028). The 2 methods checked fairly well on most coal ash fusing below 2600° F. by the gas furnace method, but very refractory ash, fusing above 2600° F. by the same method, gave much lower results by the micropyrometer method. Tentative revision was made of standard methods of lab. sampling and analysis of coal (D22-21), and of the tentative method of test for fusibility of coal ash (D22-19T). J. L. WILEY

Carbonization of coal with blue gas and producer gas. W. R. MORRIS. *Blast Furnace Steel Plant* 11, 22-30(1923).—The results obtained from the blue-gas and producer gas plant operation at the Seaboard By-Product Coke Co., Jersey City, are given; comparisons are made of their over-all economy; and consideration is given to the advantages and utility of each type of plant as adjuncts to a by-product coke plant. The advantages of producer gas over blue gas are: only 76.3% as much fuel is required per ton of coal carbonized; labor requirements are only 1/3 as much; continuity of operation is greater; the mfg. cost is about 40% less; and lower grades of fuel can be used. The

mixing of blue gas and producer gas with coal gas to obtain a specified B.t.u. can be done with equal ease.

J. L. WILEY

**Nitrogen distribution in verticals.** C. H. STONE. *Gas Age-Record* **51**, 241-3 (1923).—Previous work is reviewed and a 12-hr. test at Rochester, N. Y. on an installation of U.G.I. verticals is described. The coal showed 1.75% N, and the coke 1.16%, leaving 0.94% of the wt. of the coal as N to be distributed among the products of distn. The total free N in the gas was 1.73% by vol. Of the N in the products of distn. the lower hydraulic liquor and tar contain as  $\text{NH}_3$  0.10% N by wt.; tar contains as CN 0.000007%; liquor as CN 0.00045%. The upper hydraulic tar contains as  $\text{NH}_3$  0.13%; primary liquors as  $\text{NH}_3$  1.37%; tar as CN 0.00048%; primary liquors as CN 0.016%; primary tar as  $\text{NH}_3$  0.77%; primary tar as CN 0.00039%; gas as  $\text{NH}_3$  21.94%; gas as CN 2.64%; gas as N 73.01%. Twenty-four % of the possible  $\text{NH}_3$  yield was obtained.

J. L. WILEY

**Factors influencing the yield of ammonia in the carbonization of coal. II. Dissociation, the influence of water vapor and the character of the contact materials.** R. A. MOTT and H. J. HODSMAN. *J. Soc. Chem. Ind.* **42**, 4-12T, 26T, 39-40T (1923); cf. Greenwood and Hodsmann, *C. A.* **16**, 3744.—In a coal-gas atm.  $\text{NH}_3$  is measurably dissociated at 650° and completely so at 800°. This effect is prevented somewhat by the presence of water vapor; at 850° dissociation is completely arrested when 25% and probably less of water vapor is present. The presence of O in practice may promote  $\text{NH}_3$  losses by causing local heating, the reactions being very sensitive to temp., but where temps. are carefully controlled the presence of a small amt. of O retards the dissociation of  $\text{NH}_3$  owing to the formation with the H present of water vapor. In an atm. of H the dissociation is slightly less than with dry coal gas. In N the decompn. of  $\text{NH}_3$  occurs much more readily, being perceptible at 500° and complete at 660°. The catalytic activity of brick material depends largely on the amt. and conditions of the Fe present. Fused Si and, especially, C arising from the decompn. of hydrocarbons are contact materials with low activity. The decompn. taking place when coke is used as the contact material can be traced probably to the quality and quantity of the ash, since the C is a relatively inert material. Coals contg. large amts. of free  $\text{Fe}_2\text{O}_3$  might be expected to give reduced yields of  $\text{NH}_3$  in carbonizing practice.

J. L. WILEY

**Forms of specifications for purchasing coal.** HUBB BELL. *Proc. Am. Soc. Testing Materials* **22**, Part II, 567-79 (1922).

J. L. W.

**Rational basis for coal-purchase specifications.** E. B. RICKETTS. *Proc. Am. Soc. Testing Materials* **22**, Part II, 557-66 (1922).—An explanation of some of the points necessary to be considered in adopting a satisfactory specification.

J. L. WILEY

**Flotation methods successfully used in Gt. Britain to clean coal, culm, and sludge.** C. H. S. TUPHOLME. *Coal Age* **23**, 177-80 (1923).—Coal to be cleaned, after being ground until particles pass through a 0.1 linear in. aperture, is mixed with 3-4 times its wt. of  $\text{H}_2\text{O}$ , and agitated with a special reagent, approx. 1 lb. to a ton of material. This process may be applied to coking coals, low grade coals, dump wastes, stocks of slack, and washing sludge. Special reagent may be paraffin oil, cresols, oil of pine, naphthylamine, zyldine, and various tar oils. Agitation in the presence of the reagent produces a multitude of minute air bubbles, to which the coal particles attach themselves. The loaded bubbles rise to the surface of the  $\text{H}_2\text{O}$  and form a froth contg. the coal, which is removed. Material which contains a high % of ash sinks. Cost of flotation is small, approx. 9 c. per net ton of coal treated for plant having a capacity of 1000 net tons per day.

C. T. WHITE

**The coefficient of the Siegbert formula.** F. C. WIRTZ. *De Ingenieur* **38**, 13-6 (1923).—In the empirical formula of Siegbert  $V = K(T - t)/[\text{CO}_2]$ .  $V$  is the loss of heat in the chimney in % of total heat of combustion,  $T$  and  $t$  are the temp. in the chimney

and of the atm., resp., and  $[CO_2]$  is the  $CO_2$  concn. of the chimney gases. The const.  $K$  does not always equal 0.65 (as given in German books), nor 0.68 (as given in French books) but varies according to the compn. of the coal and also with the  $CO_2$  content of the gases. Diagrams are given for various coals from which can be read the change of  $K$  for variations of  $CO_2$  between 5 and 20%. This change is very considerable, as much as 60% in some cases.

R. BRUTNER

**Molasse coal.** F. O. H. BINDER. *Chem.-Zig.* **46**, 1148-9(1922).—B. describes the occurrences and working of a tertiary sub-bituminous coal on the northern and southern slopes of the Alps.

ERNEST W. THIELE

**German brown coal compared with American lignite.** O. P. HOOD. *Chem. Met. Eng.* **28**, 58-9(1923).—American lignite has approx. 35% moisture, German brown coal about 60%. The former resembles bituminous coal in hardness and appearance whereas the latter is soft and friable, distinctly earthy in appearance with sometimes a woody fiber and can be dug with a spade or chain bucket conveyor. Brown coal contains up to 13% of natural binder which is of great value in the briquetting process. The brown coal is dried to about 13% of moisture and forced under high pressure through a converging die, which generates sufficient heat by friction to melt the inherent binder and thus waterproof each particle. Lignite contains less than 1.5% of binder and therefore our briquetting problem is fundamentally quite different from that of the German brown-coal industry. The brown-coal briquets, having a heat value of about 8600 B. t. u. per lb. make an excellent fuel for industrial and domestic consumption. Three tons of brown coal make 1 ton of briquets, 1 ton of the raw material being required to reduce the other 2 tons to 1 of briquets. The raw brown coal has a limited use as industrial fuel on step grates where transportation for long distances is unnecessary. In 1921, 123 million tons of raw coal and 28 million tons of briquets were produced. Also in *Power* **57**, 63-4(1923).

J. L. WILEY

**Rosedale uses bumping tables to wash its product, mixing it for coking purposes with gas coal.** G. A. RICHARDSON. *Coal Age* **23**, 285-92(1923).—A description of the Cambria Steel Co.'s coal-washing plant, "the largest and most modern of its type in the country."

E. H.

**Grudekoks.** O. P. HILL. *Coal Age* **23**, 175-6(1923).—Grudekok or lignite char is lignite from which 25-40% of the  $H_2O$  has been expelled. A typical proximate analysis is  $H_2O$  2, volatile matter 12, fixed C 72, ash 14%. It is gray black in color and very fine, 40% passing through an  $1/8$ -in. screen. In Europe this material is powdered, mixed with a suitable binder and pressed into briquets. A special stove has recently been designed for burning lignite char.

C. T. WHITE

**Lignite.** S. RUHEMANN AND O. ZELLER. *Z. angew. Chem.* **35**, 725-7(1922).—A lignite was heated electrically in a special app. to over  $500^\circ$ . When the distillate was returned to the app. and the same energy supplied in the same time, the temp. reached was  $22^\circ$  lower. Hence the reaction is exothermic. The lignite was also heated to various temps. (below  $365^\circ$ ) and held there for 6 hrs., the products being studied.  $H_2$  and  $N_2$  were absent; at  $200^\circ$  and above  $H_2S$ , some hydrocarbons, and much  $CO_2$  appeared. At  $250^\circ$  solid paraffin began to be evolved; hence lignite begins to decompose at  $200^\circ$ . The theoretical significance is discussed.

ERNEST W. THIELE

**Gas composition by calculation.** M. L. ABBOTT. *Gas Age-Record* **51**, 141-3(1923).—The  $CO_2$ , illuminants, O and CO are detd. on the Orsat app., and the B. t. u. value and sp. gr. are obtained. The following equations are then used in which C, D, E, F, B, and A denote, resp., the above values and M, H and N the  $CH_4$ , H and N to be found:  $M = 1 \div 8.6 [362 A + B - (2C + 25D + 0.47E + 3.24F + 351)]$ ;  $H = 107.7 + 0.61 C + 0.61 D \div 0.14 E - (111 A + 0.457 M)$ ; and  $N = 100 - (C + D + E + F + H + M)$ . The detn. of illuminants is discussed.

J. L. WILEY

**Manufacture of water gas.** JAMES HALL. *Gas J.* 161, 209-11(1923).—Details of the process and operating results are given for the Temple Works at Glasgow. The generating plant consists of 3 complete Humphreys and Glasgow carburetted water-gas sets of a total capacity of 3 million ft.<sup>3</sup> per day when using 2.5 gal. of oil per 1000 ft.<sup>3</sup> The gas made per ton of coke is 50600 ft.<sup>3</sup> of 296 B. t. u. at a thermal efficiency of 57.5%. The B. t. u. is raised to 450 by carburetted with 1.5 gal. of oil per 1000 ft.<sup>3</sup> The cost per therm is 3.95 d.

J. L. WILEY

**Heat economy in the water-gas process.** KRONENBERGER. *Gas u. Wasserfach* 65, 745-52(1922); cf. Geipert, *C. A.* 17, 462.—The total heat consumption in the water-gas process becomes greater as the generator temp. and the CO<sub>2</sub> content of the water gas increase. The heat efficiency can be improved by reducing the CO<sub>2</sub> content of the water gas or the temp. in the generator by correctly proportioning the steam to the generator per unit of time and per sq. m. of generator cross-section or the periods of blow and gas-making to each other. Furthermore, the utilization for power purposes of the sensible and combined heat in the blast gases and in the water gas leaving the generator by means of waste-heat boilers should not be overlooked. K. shows the value and significance of these various factors by quoting in some detail and by means of charts the data obtained from carefully made plant tests.

J. L. WILEY

**By-product oven heat balance.** D. S. CHAMBERLIN AND E. W. MCGOVERN. *Gas Age-Record* 51, 199-202(1923).—Data and calcs. are given in detail of a heat balance obtained from a battery of 106 Koppers ovens. The available heat input is divided as follows: latent heat in coal 88.71%, sensible heat in coal 0.01, latent heat in fuel gas 8.53, sensible heat in fuel gas 0.01, sensible heat in preheated air 4.74; the heat distribution: latent heat in coke 61.51%, sensible heat in coke, 3.55, latent heat in fuel gas 19.33, sensible heat in fuel gas 1.26, total heat going out stack 3.16, latent heat in tar 3.85, sensible heat in tar 0.05, heat absorbed in tar formation 0.13, radiation and convection losses 1.14, latent heat in light oil in fuel gas 0.86, unaccounted for 5.16. The heat required to coke 1 lb. of dry coal is 804.9 B. t. u. A check run on a battery of Semet-Solvay ovens showed a B. t. u. value of 788, amounting to a heat loss of 5.06%.

J. L. WILEY

**Determination of benzene in gases.** E. BERL. *Z. angew. Chem.* 35, 332(1922).—Adsorption in charcoal is superior to oil absorption for analytical as well as for technical processes. A preliminary treatment with a small proportion of oil, followed by passage over charcoal, increases the recovery of benzene greatly over that of the straight oil process.

W. F. FARAGHER

**Lime consumption in sulfate of ammonia manufacture.** H. J. HAILSTONE. *Gas J.* 161, 331(1923).—A graphic chart is given for ascertaining the correct rate of liquor feed and lime addition for a given output, with liquors of all strengths from 1 to 4 oz. fixed NH<sub>3</sub> and 7 to 12 oz. total NH<sub>3</sub>.

J. L. WILEY

**Thermal efficiencies of production of different grades of gas.** A. PARKER. *Gas J.* 161, 334-6(1923).—A general review of the work already accomplished by the Institution of Gas Engineers. Cf. *C. A.* 14, 2409; 15, 2709; 16, 2771.

J. L. WILEY

**Rust dust causes meter troubles.** JAMES FERRIER. *Gas Age-Record* 51, 203-4(1923).—Deterioration of meters is due to the accumulation therein of rust charged with cyanides. The remedy is to purify the gas of cyanides and to install a dust catcher in the pipe before the meter.

J. L. WILEY

**Application of diffusion to gas analyses.** ANON. *Gas J.* 161, 336-7(1923); cf. Ringrose, *C. A.* 15, 2978.

J. L. W.

**Trend in blast-furnace gas cleaning.** F. E. KLING. *Blast Furnace Steel Plant* 11 44-6(1923).—The advantages of dry-hot cleaning over wet-cold cleaning are discussed and the Halberg-Beth and Kling-Weidlein processes of dry cleaning are compared.

The advantages of initial and operating costs, ground space, power and labor required, temp. of clean gas, and life of filter lie with the latter type. J. L. WILEY

**Experience with producer firing.** S. B. SHERMAN. *Gas Age-Record* 51, 139-40 (1923).—Results are given of 15 months' experience in firing 50 benches of 6's consisting of 12-ft. through-horizontal-retorts. A large saving in labor and fuel is reported and the ability to attain a slightly higher temp. in the benches and to carry a more uniform heat. J. L. WILEY

**Aid to the calculation of mean spherical and mean hemispherical candle powers.** A. R. MYHLL. *Gas J.* 161, 332-3 (1923). J. L. W.

**Economic factors of gas production and distribution.** H. L. BATEMAN. *Gas J.* 161, 337-8 (1923). J. L. W.

**Recording gas calorimeters and their use.** J. W. WOOD. *Gas J.* 161, 205-9 (1923).—The paper calls attention to points which should be considered in the examn. of a recorder and the detn. of its suitability and accuracy for use in specified circumstances. J. L. WILEY

**Primary tar and primary tar residuum.** J. MARCUSSEN AND M. PICARD. *Z. anorg. Chem.* 35, 493-4 (1922); cf. *C. A.* 15, 3386; Tropisch, *C. A.* 15, 3550.—The characteristic property of carboxylic acids is a sapon. no. about double the acid number. The assertion that phenolcarboxylic acids form phenols on distn. with  $\text{PhNH}_2$  has not been found true. By heating at  $180^\circ$  and under pressure an ethereal soln. of carboxylic acids contg. piperidine splits off the COOH group and the product previously sol. in NaOH becomes insol. However, phenolcarboxylic acids do not become sol. as expected because of lactone formation. Primary tar residuals were found superior in usefulness in the building industry. Outwardly the carboxylic acids of coal tars resemble humic acids, found to possess inner anhydrides as well as free COOH groups. The ether-sol. acids of primary coal tar are identical with acids separable from beech wood tar, which from its formation from lignin or cellulose must be close to humic acid, and must also bear a like relationship. Analyses of 2 tars, a neutral coal-tar resin, pitch and resin from lignite tar and a table of physical properties of these tars are given. R. L. BROWN

**Crude tar.** I. FRANZ SCHÜTZ. *Ber.* 56B, 162-9 (1923).—This investigation concerned itself with the investigation of that part of the light oil from anthracite coal, b. between  $28-75^\circ$ , most of the article dealing with methods of sepn. and identification. This low-boiling fraction contains small amts. of the paraffin hydrocarbons, somewhat larger amts. of the unsatd. hydrocarbons but the principal part consists of aromatic and hydroaromatic hydrocarbons, of which  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$  and  $\text{C}_6\text{H}_4\text{Me}_2$  were identified and higher members of the series were probably present. The absence of  $\text{C}_{10}\text{H}_8$  was established. Ketones were also present, especially  $\text{AcMe}$ .  $\text{PhOH}$  occurs in larger amts. than in coke-oven tar. Traces of  $\text{AcH}$  and  $\text{MeCN}$  were also found. C. J. WEST

**Coke.** RICHARD MOLDENKE, et al. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 463-5 (1922).—Report of Comm. D-6 in regard to detg. the phys. properties of coke. Tentative revision was made of standard methods of lab. sampling and analysis of coke (D37-21). J. L. WILEY

**Manufacture of  $(\text{NH}_4)_2\text{SO}_4$  (GRIEBEL) 18.** Density of a mixture of O, CO and  $\text{CO}_2$ . Relation between the volume percent and weight percent (SCHREIBER) 2.

**Fuel mixture.** L. R. GARLOCK. U. S. 1,444,341, Feb. 6. A mixt. of benzine 48, kerosene 47.9, ether 3.5 and  $\text{KNO}_3$  0.6 part is used as a fuel for internal-combustion engines.

**Gaseous fuel.** J. R. ROSE. Can. 227,534, Jan. 2, 1923. A gas mixt. for cutting and welding contains H 5% with  $\text{CH}_4$  20%.

**Gaseous fuel.** JNO. HARRIS. Can. 227,530, Jan. 2, 1923. H 95-50% is mixed with artificial illuminating gas 5-50%. In 227,531 carbureted water gas replaces the illuminating gas of the prior pat. In 227,532 CO is mixed with H in the above proportions. In 227,533 H and  $C_2H_4$  are mixed.

**Liquefied gaseous fuel mixture.** C. F. CROMMETT. U. S. 1,444,665, Feb. 6. C powder is suspended in liquefied natural gas or other liquefied normally gaseous hydrocarbon material, to form a mixed fuel adapted for use with blow-pipes for cutting or welding metals.

**Stable liquid fuel mixture.** L. W. BATES. U. S. 1,444,723 Feb. 6. Coal is pulverized so that 85% of it will pass a 200-mesh screen, mixed with a liquid hydrocarbon fuel, and a stabilizing substance, *e. g.*, lime-rosin grease and coal distillate, and "suspension-sized" particles are removed from the mixt. by centrifugalizing, dln. and sedimentation or filtration to obtain a stable mixt. adapted for use as a fuel in engines. Cf. C. A. 16, 156.

**Coked mixed fuel.** C. I. GILLSTRAP. U. S. 1,443,359, Jan. 30. A mixt. of ground lignitic material, clay, coke and a tar binder is coked at 500-1000°.

**Distilling and burning fuel on a traveling grate.** B. MEYER. U. S. 1,443,632, Jan. 30. Fuel such as coal is fed through a distg. chamber on to a traveling furnace grate and a sufficient amt. of the combustion gases is led through the distg. chamber to form  $NH_3$  and low-temp. tar. Distn. products are cooled and cleaned to recover by-products and residual gases are led back to the combustion chamber of the furnace.

**Briquets from peat.** E. C. WALLACE. U. S. 1,443,105, Jan. 23. Partially dried peat still contg. 50-65%  $H_2O$  is mixed with powdered coal or sawdust and cement, briquetted and dried.

**Determination of naphthalene in illuminating gas.** W. H. FULWEILER. U. S. 1,443,330, Jan. 23. A measured amt. of the gas is passed through a standard picric acid soln. to convert its  $C_{10}H_8$  content into  $C_{10}H_8$  picrate and increase the elec. resistance of the soln. and the change in elec. resistance is utilized for estg. the amt. of  $C_{10}H_8$ .

**Vertical gas retort and producers.** J. W. DRAKE. U. S. 1,444,498, Feb. 6. Two gas producers adjoin a vertical retort and a passage leads from each of the producers to a chamber common to and intervening between the retort and the producers. Another passage leads from the chamber mentioned to a chamber surrounding the vertical retort. A duplex valve is mounted between each of the producers and the chamber first mentioned.

**Automatic governor for gas producers.** G. R. McDERMOTT. U. S. 1,444,383, Feb. 6. A blast-blower of a gas producer is steam-driven and the supply of steam for driving the blower is automatically controlled by back pressure to maintain a uniform flow of air.

**Apparatus for generating water gas by use of coal dust.** H. BATCHELOR. U. S. 1,442,993, Jan. 23. Two main generators each filled with refractory material such as porous baked fire-clay are connected with a receiver generator, similarly filled, so that gas from one main generator heats the receiver generator while the other main generator is being charged.

**Apparatus for scrubbing coal gas.** A. F. MESTON. U. S. 1,444,627, Feb. 6. The gas to be treated is passed in succession through an absorption chamber, a spray chamber and an elec. precipitator, arranged one above another.

**Paraffin and lubricating oils from crude bituminous tar.** E. ERDMANN. U. S. 1,443,983, Feb. 6. Cold crude bituminous tar (*e. g.*, lignite tar) is treated with acetone and the soln. thus formed is filtered off from paraffin which seps.; the paraffin is dissolved in tar oils or other inert solvent and the soln. so obtained is treated with concd.  $H_2SO_4$ ;

acid resins and the  $H_2SO_4$  are removed from the soln. and the paraffin is pptd. by the action of acetone. The oil residue, distd. with steam, is adapted for use as lubricating oil.

**Briquetted coke.** W. E. DAVIES. U. S. 1,443,618, Jan. 30. Up to 10% of a resinous binder such as resin or bituminous matter is added to coal and the mixt. is formed into briquets (which may be perforated) and the latter are partially carbonized under reduced pressure.

**Upright coke-oven or carbonizing furnace structure.** G. A. BALZ. U. S. 1,443,161, Jan. 23.

## 22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

**Specifications for petroleum products and methods for testing.** Federal Specifications Board, Standard Spec. No. 2. Bur. of Mines, *Tech. Paper* 323, 88 pp. (1923).—Official U. S. government specifications are given for gasolines, naphthas, burning oils, fuel oils and lubricants, and methods are given for testing for various purposes a variety of petroleum products.

E. J. C.

**Refining the more important types of crude petroleum.** RICHARD KISSLING. *Chem.-Ztg.* 46, 541-4, 562-5 (1922).—A general discussion of technical methods of distg. and refining typical crude oils.

W. F. FARAGHER

**Rocky mountain crudes.** F. B. TAYLOR. *Oil & Gas J.* 21, No. 36, 98-9 (1923).—The producing fields of the Rocky Mt. region are listed and classified as to geological period, av. daily production, and kind of crude. Data on the pipe lines of this region are also given.

D. F. BROWN

**Cloud and pour test (petroleum products).** T. G. DELBRIDGE, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 442-4 (1922).—Changes in the Tentative Test for Cloud and Pour Test of Petroleum Products are recommended.

W. F. FARAGHER

**Design and operation of a low-pressure absorption plant.** W. P. DYKEMA AND A. A. CHENOWETH. Bur. Mines, *Tech. Paper* No. 263, 42 pp. (1922).—Construction, operating methods and difficulties encountered in a plant in the Cushing field handling a rich casing-head gas are described and discussed critically. The second part (11 pp.) contains observations on the effect of the latent heat of rich gases in absorber towers, and on methods for cooling the gas or absorbent oil.

W. F. FARAGHER

**Sulfuric acid treatment of petroleum products.** C. J. VON BIERA. *Chem. Met. Eng.* 27, 66-72 (1922).—A review of the chem. reactions and plant practice in acid refining.

W. F. FARAGHER

**Color of petroleum products.** T. G. DELBRIDGE, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 425-9 (1922).—Report of sub-committee on test for refined oil, Saybolt chromometer being used. Tables for Saybolt colors matched by solns. of  $K_2Cr_2O_7$  are included. A set of  $K_2Cr_2O_7$  solns. matching the N.P.A. colors is presented. W. F. F.

**Cost of producing natural-gas gasoline.** E. C. SIEVERS. *Chem. Met. Eng.* 28, 297-8 (1923).—The scope of the industry is briefly outlined and recovery costs for various types of plants are analyzed.

E. J. C.

**Natural gas gasoline in 1921.** E. C. SIEVERS. U. S. Geol. Survey, *Mineral Resources of U. S., 1921*, Pt. II, 237-52 (Preprint No. 30, publ. Jan. 25, 1923).

E. J. C.

**Effect of small quantities of volatile impurities on the flash-point of kerosene.** E. C. CRAVEN AND B. G. BANKS. *J. Inst. Petroleum Tech.* 8, 490-9 (1923).—Kerosene may contain traces of very volatile substances, probably unsatd. in character, which lower the flash-point when detd. by means of the Abel or similar tester. These volatile con-



stituents are partially adsorbed by powdered coal, animal charcoal, etc., and the true flash-point of the kerosene is established. The difference between the Abel flash-point, and that of Ormandy and Craven (*Ibid* 8, 151(1922); *C. A.* 16, 1147) is the measure of the volatile material present. Tables are given. W. F. FARAGHER

**The scope of the conception, "mineral-oil."** D. HOLDR. *Chem.-Ztg.* 46, 501-4 (1922).—As the result of a controversy between dealers in petroleum and its products and mfrs. of oils from brown coal and shale, the following definition for mineral oil was proposed in the section on mineral oil at the recent annual meeting of the Society of German Chemists: Mineral oils are products which are used technically. They receive the designation in order to set forth their contrast to animal and vegetable oils, in point of source, etc. They are obtained from minerals sources, and it is wholly immaterial whether they are obtained from imbedded or incrustated deposits, as primary substances, *e. g.*, petroleum, or whether they are produced as secondary products by the more or less complete destructive distn. of such substances as coal, shale, etc. It is demanded that chemically they be aliphatic or naphthenic compds. Final decision on the scope of the term has been delegated to a sub-committee. H. presents a discussion of usage in Germany, showing that many brown-coal and shale products, as well as coal-tar products from which phenols have been removed, are classed as mineral oils. On the other hand, important producers of these products have used a descriptive name, indicating the source of the material, such as "shale-oil lubricant." Perhaps in the majority of instances, the term, if unmodified, is considered to refer to petroleum and its products. The controversy hinges on the quality of the respective classes of products. If there were no differences in quality and in general chemical characteristics, the objection to an inclusive class name would not exist. This situation is found in the case of synthetic indigo and alizarin, and in that of paraffin wax from brown coal or shale. The chemical limitation is unacceptable, since many crude petroleum contain considerable percentages of aromatics. W. F. FARAGHER

**Problem of durability tests for transformer oils.** T. G. DELBRIDGE. *Proc. Am. Soc. Testing Materials* 22, II, 532-40(1922).—The estd. consumption of transformer oil in the U. S. during 1921 is 15 million gal. The market value of this oil is 2 million dollars. The initial requirements of an oil are well understood, with the exception of those controlling the durability of the oil under service conditions. Exclusion of air is desirable when a design permitting this practice is possible. Improvement of the quality of turbine oil by proper refining is possible, but it is unlikely that elimination of the evils arising from slow oxidation can be effected in this way. The various durability tests in current use are discussed briefly. It is hoped that an entirely satisfactory test will be developed soon by the cooperative work of committee D-9 of the Am. Soc. for Testing Materials. W. F. FARAGHER

**Procedure for the transformation of hydrocarbons of high molecular weight into hydrocarbons of low molecular weight.** A. MAILHE. *Rev. sci.* 24, 825-30(1922).—The following processes are briefly outlined: (1) cracking, (2) destructive distn., (3) catalytic, with Cu as a catalyst, (4)  $AlCl_3$ , and (5) hydrogenation under high pressure (200 atm.). C. T. WHITE

**Cracking of hydrocarbons by aluminium chloride.** A. MAILHE. *J. usines gas.* 47, 33-6(1923).—A general survey. J. L. WILEY

**Mutual solubility of hydrocarbons, fatty oils, and liquid sulfur dioxide.** E. ZERNER, H. WEISS AND H. OPALSKI. *Z. angew. Chem.* 35, 253-6(1922).—Contrary to the statement of Moore, Morrell and Egloff (*C. A.* 12, 1923),  $PhCH_3$  is not completely miscible with liquid  $SO_2$  at  $-10^\circ$ . Table III of M., M., and E.'s paper is said to be contrary to the laws of soly., since the relative proportions of two partially miscible liquids in a system cannot affect the concn. of the two liquid layers at a given temp. (Z., W., and O.

have misinterpreted the method used in expressing soly. in this table. However, the data seem to be slightly irregular.—W. F. F.) Likewise, the method used by M., M., and E. is criticized as being inaccurate. The critical soln. temps. of weighed mixts. of toluene, *n*-tetradecane, decahydronaphthalene, tetrahydronaphthalene, a fraction of American petroleum ( $d_{40} 0.8102$ ,  $n_D^{25} 1.4514$ , 94.4% distg. between 175 and 250°), castor oil, olive oil, rape-seed oil, linseed oil, tallow, and bone grease. Tubes of resistance glass, such as are used for boiler sight-gages, were employed. The tubes were tested at a pressure of 12 atm., and could be used, therefore, at temps. as high as 55–60° with liquid  $SO_2$ . The temps. at which soly. was complete were checked by cooling and noting the sepn. of the first undissolved substance. The data on fatty oils are included because of a possible interest in extn. processes (Grillou and also Schröder have old patents). The soly. of fatty oils increases with the degree of unsatn. The OH group of castor oil makes its soly. high.  $SO_2$  is sol. in the various oils, both mineral and fatty. W. F. F.

**Production increased and cost lowered by towers.** J. C. CHATFIELD. *Nat. Petroleum News* 14, No. 43, 55–6(1922).—The addn. by the Pure Oil Co. of towers to the continuous stills decreased the operating expense 3 cents per bbl., increased the still capacity 33 1/4%, increased the gasoline recovery 2.86% and decreased the loss from 2.63% to 0.78%. The towers are 5 ft. in diam. and 30 ft. high and are a combination of the baffle plate and "crock" types. After passing one series of baffles the vapors pass through 6 tiers of staggered, unglazed stone jars before reaching a second series of baffles through which it moves to another series of jars before reaching the outlet line running to the condenser box. D. F. BROWN

**A section through the New Albany shale.** J. A. REEVES. *Bur. of Mines, Repts. of Investigations* No. 2425, 3 pp.(1922); cf. C. A. 17, 205.—A boring was made in Clark Co., Ind., and the core divided into 31 sections of approx. 3 ft. each. The av. yield of oil for the upper 50 ft. is 11.6 gal. per ton; between 50 and 60 ft. the yield is very low; while from 60 to 98 ft. it averages 7.0 gal. per ton. That the oil-forming material of the shale is of the same compn. throughout its depth is shown by the small variation in sp. gr., and the amt. of tops from the crude oil. C. T. WHITE

**Recent experimental work in the Rosevale (Baltimore, N. B.) oil shale area.** W. S. McCANN. *Can. Dept. Mines, Memoir* 129, 56–60(1922).—The plant used though complete in itself is a unit of a possible future plant of much greater capacity. It is designed to treat oil shales by the Wallace process. The charge of about 1000 lbs. of shale is heated in the retort for 3 hrs. at approx. 730° and steam is injected into the retort during the process. The volatile constituents are withdrawn by vacuum from the inner duct of the retort to water-cooled condensers where the oil is sepd. and the other gases are carried to the ammonia scrubber plant. A comparison of yields by the Wallace retort with the Scotch tube methods gave an av. of 2.5 gal. in favor of the former. The working data of this plant are given. L. W. RIGGS

**The possibility of isolating bitumen in its original condition from bituminous shales.** E. HENTZE. *Z. angew. Chem.* 35, 330–1(1922); cf. C. A. 16, 2598.—The sepn. of bitumen and mineral constituents of a diatomaceous earth and of a shale, kukersite, was attempted in the following way. About 2 kg. of each mineral was treated for 14 days with dil. HCl at ordinary temp. Every 24 hrs. the acid soln. was filtered off and the residue washed with lukewarm water until tests for  $Ca^{++}$  and  $Fe^{++}$  were negative. Fresh acid was then added. After  $Ca^{++}$  and  $Fe^{++}$  were removed as thoroughly as possible, a similar treatment of the residue with dil. HF and then with 40% HF followed. The latter treatment required 4 weeks for kukersite and 2 weeks for the earth. A deep olive-green, pasty, residue was obtained from the earth. It dried quickly and could then be rubbed to a powder. The removal of mineral constituents was, however, incomplete in each case. The residues were accordingly extd. with  $CHCl_3$ , the best solvent for these

products. After evapn. of the  $\text{CHCl}_3$ , a stiff, plastic, olive-green residue remained from the diatomaceous earth sample. The ext. from kukersite was dark brown and also plastic. Not all the bitumen was recovered in this way; 58 g. out of a possible 80 g. was the recovery from kukersite. Portions of these bitumens were mixed with  $\text{SiO}_2$  or with clay and lime (same percentages as those of the mineral constituents in the original), and distd. from a glass retort. The percentages of volatile products obtained were smaller than those from the minerals themselves. The decrease was 1% for diatomaceous earth and 5% for kukersite. Likewise, the percentages of low-boiling constituents recoverable from the tars were increased. The coke from the recovered bitumen had a higher % of C than that from the mineral itself. These differences indicate that the original bitumen was not isolated by the process used, and the changes are attributed to polymerization. The "cracking" of the polymers gives rise to the increased percentages of low-boiling products. The possibility of sepg. the bitumen by electroösmosis is good. Microscopical examn. of a number of shales shows that the bitumen is associated with clay, and that the latter functions as a protective colloid. An org. solvent, to which the requisite amt. of electrolyte and of thickening agent (to raise the sp. gr. to that of the mineral) can be added, is not easily discovered for the process. Possibly, suspensions which can be used directly can be made by Plauson's colloid-mill.

W. F. FARAGHER

**Petrolatum.** F. R. BAXTER, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 419-21 (1922).—Report of sub-committee on melting point detn. of petrolatum.

W. F. FARAGHER

**Gasoline.** T. G. DELBRIDGE, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 446-51 (1922).—Report of sub-committee. Tables showing tests by coöperating labs. are given as follows: sp. gr., distn., S detn., I no., "Doctor" test, gum by Cu dish method, and Cu strip corrosion test.

W. F. FARAGHER

**Paraffin wax.** C. K. FRANCIS, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 422(1922).—A proposed method for detg. oil and moisture in paraffin wax is presented by the sub-committee on paraffin wax.

W. F. FARAGHER

**The shale-oil industry of Scotland.** EDWIN M. BAILEY. *J. Inst. Petroleum Tech.* 8, 465-90(1922).—A complete but concise description of the equipment and processes of a Scotch shale-oil plant is given.

W. F. FARAGHER

**The composition of commercial paraffin.** A. W. COSTER VAN VOORHOUT. *Chem. Weekblad* 19, 566-9(1922).—Com. paraffin, m. 60.3°, fractionated by vacuum-distn. (pressure not given) gave at 334-50° 59.7% of the total amt., m. 57.9°, and at 350-73° 37.5%, m. 62.9°. Crystn. from amyl alc. at 36° gave 57% of the total amt., m. 63.2°; at 26°, 13%, m. 61.4°. Crystn. from amyl alc. and ethyl alc. mixt. at 28.5° gave 2.5%, m. 58.2°; at 16°, 14.3%, m. 57.3°; at 0°, 12.1%, m. 56.6°. R. BEUTNER

Geology of the Moncton map-area (WRIGHT) 8. A new compound from coniferous wood distillates (CEDERQUIST, HOLMBERG) 10. Raphaelite (LONGOBARDI) 8.

**Cracking hydrocarbon oils.** W. F. MUEHL. U. S. 1,444,128-9, Feb. 6. Oil of relatively high b. p. is heated to a cracking temp. in a preheater through which the oil is passed upward (through vertical tubes) at such a rate as to restrict cracking in the preheater. The preheated oil is passed from the top of the preheater to a horizontal elongated insulated digester, through which the oil passes from end to end in a state sufficiently quiescent to maintain it at cracking temp. for some time without further heating, to permit C deposition, cracking and vaporization of products of low b. p., under pressure. C is scraped from the bottom of the digester to one of its ends and removed and unvaporized oil overflowing from the outlet of the digester is led back for reheating

and further conversion. Vapor from the digester is led to a dephlegmator to the base of which fresh oil may be fed; this together with condensates overflows from a pool in the base of the digester to a second digester. A vapor discharge pipe from the latter leads to the dephlegmator and the 2 digesters are connected so that unvaporized oil may be passed from the first to the second digester.

**Cracking petroleum oils.** L. C. READ. U. S. 1,445,040, Feb. 13. Heavy petroleum distillate or other hydrocarbon oil to be treated is first heated to about 1100° in a pipe coil under a pressure less than atm. pressure to cause conversion and is then subjected to an increased pressure at a lower temp. to effect further conversion.

**Oil refining.** H. PLAUSON. Can. 227,885, Jan. 9, 1923. Oily material is emulsified with water to form a filterable emulsion from which the impurities are removed by ultra-filtration at high pressure.

**Distilling gasoline from other fractions.** H. F. PERKINS. U. S. 1,444,208, Feb. 6. A hydrocarbon mixt. contg. a gasoline fraction is distd. and the vapors are cooled to a temp. lower than the initial b. p. of the residue to be obtained; the cooled uncondensed vapors are passed through a dephlegmator in contact with condensate and are cooled to substantially the dry point of the gasoline to be obtained and condensed.

**Apparatus for petroleum distillation.** C. B. FORWARD. U. S. 1,442,935, Jan. 23. Oil is preheated in pipe coils and then treated with superheated steam to effect production of a "motor fuel" from heavier oil.

## 23—CELLULOSE AND PAPER

CLARENCE J. WEST

**A cheap and interesting solvent for cellulose esters.** ALBERT HUTIN. *Rev. chim. ind.* 31, 141-3(1922).—Brief discussion of the merits of EtOAc. A. P.-C.

**Saccharification of cellulose.** P. P. BUDNIKOV AND P. V. ZOLOTAREV. *Bull. Inst. Polyt. Ivanovo-Voznesensk* 4, 119-28(1921).—When dry filter-paper is saccharified by treating it with cold 72% H<sub>2</sub>SO<sub>4</sub>, then dilg. the transparent soln. obtained until it contains only 3% of acid, and heating this in an autoclave at 120° for two hrs., the percentage of dextrose in the resulting liquid does not exceed 0.6. The concn. of the sugar may, however, be increased by dilg. the strongly acid soln., not with water, but with dextrose soln. previously obtained in the same way and freed from H<sub>2</sub>SO<sub>4</sub>. When a soln. contg. 1% of dextrose and 3% of H<sub>2</sub>SO<sub>4</sub> is introduced into the cathode chamber of an electrolytic cell and the anode chamber, sepd. by means of a porous pot, is charged with water acidified with H<sub>2</sub>SO<sub>4</sub>, electrolysis should result in the collection of all the acid in the anode chamber; with a suitable porous pot, as much as 91.5% of the acid was sepd. by this method. J. C. S.

**Factors influencing the properties of wood cellulose as isolated by the chlorination method.** M. W. BRAY AND T. M. ANDREWS. *Paper Trade J.* 76, No. 8, 47-9(1923).—This study was made with the idea of establishing a method of analysis of cellulose whereby consistent results might be obtained for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cellulose and also to establish the relation of these values to other chem. consts. as well as to the character of the pulps resulting from changes in the cooking conditions and processes. Overchlorination of cellulose increases the % of nonresistant cellulose at the expense of the resistant portion. The % of 17.5% alkali-sol. cellulose repptd. by acid in sound wood and pulp is very small compared with that which exists after chlorination. The action of some organisms of decay produces the same effect on the character of the cellulose as overchlorination. There is a definite relation existing between the % of nonresistant cellulose from spruce sulfite pulp and the Cu no. The reducing power of nonresistant cellulose towards Fehling soln. is approx.  $\frac{1}{3}$  that of dextrose. C. J. WEST

**Semi-cooked pulp.** I. ENGZ. *Wochbl. Papierfabr.* **54**, 245-6(1923).—Improved methods for the prepn. of semi-cooked pulp are discussed. Wood subjected to treatment with  $\text{NaHSO}_3$  sol or spent liquors and steaming yielded, after bleaching, a good printing paper. J. L. PARSONS

**Chemistry of the sulfite process. III. Reactions of the calcium base.** R. N. MILLER AND W. H. SWANSON. *Paper Trade J.* **76**, No. 9, 49-51(1923); cf. *C. A.* **16**, 3389.—This paper records a study of the conditions influencing the disappearance of the base during the process of digestion. In some cases the decrease in base amts. to 50% of that originally present in the liquor. Some base is pptd. upon the heating coils and some removed in the cooking as relief and samples. The presence of nearly half the base in the pulp shows that it is localized around the fibers in some way. This localization varies inversely as the moisture content of the wood. The decrease is greatly reduced with a slow temp. rise during the cooking process. It appears that, other conditions being equal, the same proportion of the base disappears regardless of the acid compn. All other conditions being equal the wood of high moisture content will give a larger yield of pulp, though requiring a longer cooking time. C. J. WEST

**Rapid technic for estimating pulp fibers.** EASTMAN KODAK CO. *Paper* **31**, No. 17, 14(1923).—The paper or pulp is well pulped in the usual way, a drop or two transferred to a clean microscope slide by means of a pipet with exit of wide diam. (4-5 mm.) and the fibers are allowed to dry on the slide by heating at  $50^\circ$ . The fibers are then moistened with a drop of water and the excess is removed by absorbing it at the edge with filter paper. Stain is then added, cover glass placed on top and excess stain squeezed out. Reasons for the various steps are given. C. J. WEST

**New methods for the disintegration and refining of plant fibers.** P. WAENTIG. *Wochbl. Papierfabr.* **54**, 23-5; *Papierfabr.* **21**, 49; *Zellstoff u. Papier* **3**, 1-7(1923).—A review of war-time and post-war developments in the sulfite and soda cooking processes, with brief statements in many cases as to their merits. Mention is made of the utilization of hemp, straw, and reeds for the manuf. of paper. The use of  $\text{CO}_2$  in a recently developed combined acid-alk. bleaching process is briefly discussed.

J. L. PARSONS

**Degree of beating and hydration.** C. G. SCHWALBE. *Wochbl. Papierfabr.* **54**, 22-3(1923).—A review of the conditions influencing hydration phenomena in the beater, as well as in the sulfite and soda cooking processes. Methods of detg. hydration are listed. The time factor is important since in some cases the degree of hydration decreases after 6 or 9 hrs. Mucilage formation is markedly influenced by the temp., dissolved salts and drying. The importance of colloid chemistry is emphasized.

J. L. PARSONS

**Wood as a raw material for the manufacture of paper.** HOYER. *Papierfabr.* **21**, 17-21(1923).—General information, especially regarding economy and paper-making qualities, is given for the following woods: spruce (*Picea excelsa*), Scotch fir (*Pinus sylvestris*), fir (*Abies pectinata*), larch (*Larix europaea*), aspen (*Populus tremula*), birch (*Betula alba*), beech (*Fagus sylvatica*), linden, oak, and alder. Wts. per m.<sup>3</sup> of certain woods and their ash contents are tabulated. Woods grown in northern countries or at high altitudes are preferable for paper-making on account of their superior quality fibers. The av. length of summer wood fibers is given as 3.5-4.5 mm., width of fiber 0.03-0.06 mm., fiber wall thickness 0.002-0.003 mm.; the corresponding values for spring wood fibers are 2.5-3.5 mm., 0.015-0.03 mm., and 0.005-0.008 mm. J. L. PARSONS

**Paper pulp recovery.** L. M. BOOTH. *Paper Trade J.* **76**, No. 8, 54-5; *Paper* **31**, No. 19, 11-13(1923).—Tests extending over 31 days in a mill using rag stock showed an av. loss of 2.4 lb. per thousand gal. of white water from No. 1 machine, the min. being 0.18, the max. 7.1 lb., and an av. of 1.5 lb. from No. 2 machine. Application of *Boothal*

to recovery of this material is discussed. Boothall coagulates the fine pulp and clay or other loading materials present, thus causing more rapid settling. The effect of the formation of  $\text{Al}(\text{OH})_3$  ppt. is to prevent the adhesion of the stock to the tanks, piping, etc. The cost of operation is from 0.5 to 1 cent per lb. of recovered stock. C. J. W.

**Destruction of paper by ink.** W. HIRZBERG. *Wochbl. Papierfabr.* 54, 104-5 (1923).—Paper which was written on in 1898 with document ink and kept in a cabinet under normal conditions showed in 1921 that the ink had strongly attacked the fibrous material. Tests showed that an ink line only  $\frac{1}{4}$  mm. wide noticeably affected the strength of the sheet, while a line 2 mm. wide caused a decrease in strength of one-half. Further tests are planned to determine the injurious constituents of the ink. Also in *Mitt. Materialprüfungsamt* 40, 90-5(1922). J. L. P.

**Investigation of problems in coloring in the paper mill laboratory.** W. C. HOLMES. *Paper Trade J.* 76, No. 6, 45-6(1923).—The paper chemist should investigate practical aspects of possible modifications in coloring practice. Two factors to be studied are what provisions, practicable in beater operation, will insure a max. absorption of dye and the relative characteristics of different metallic lakes of the dyes. Cf. C. A. 17, 884.\* C. J. WEST

**Coloring of paper stock with color lakes.** EMIL HEUSER AND HANS G. BEHR. *Papierfabr.* 21, 1-6; *Paper* 31, No. 18, 7-12(1923).—The absorption of acid dyes is approx. the same for loaded paper stock as for stock free from loading materials. Basic and substantive dyes, however, are more readily absorbed by loaded stock. With basic dyes, the color is most firmly fixed by Mg silicate; next in order comes Ca silicate and finally Al silicate; with substantive dyes the order of greatest absorption is Al, Ca and Mg silicates. Acid silicates absorb basic dyes the best but substantive dyes can be used. In general, increased retention of the filler is effected by the choice of the proper dye-stuff. Exptl. data are given in detail. J. L. PARSONS

**Colloid chemistry of paper sizing.** RUDOLF LORENZ. *Papierfabr.* 21, 54-6; *Zellstoff u. Papier* 3, 7-10; *Pulp Paper Mag. Can.* 21, 191-2(1923); *Wochbl. Papierfabr.* 53, 4542(1922).—Discussion of the action of  $\text{Al}_2(\text{SO}_4)_3$  upon colloidal rosin and the various functions it plays in sizing. J. L. PARSONS

**Degree of dissociation and unsaponifiable matter in rosin size.** A. HAUG. *Wochbl. Papierfabr.* 53, 3935-8(1922); 54, 25-7, 243-5(1923).—Na resinate, when highly dild. with distd.  $\text{H}_2\text{O}$ , undergoes hydrolysis which is approx. 100%. With city water, Na resinate yields a ppt. becoming larger on diln. Rosin milk, contg. 20% unsapon. matter, was not as highly dissociated and gave an emulsion with larger particles. Unsapon. matter brought about an easier flocculation. The presence of free rosin in a size soln. contg. Na resinate and distd. water produced no decided increase in dissociation upon diln. Beyond a definite point the dissociation dropped. The emulsion was fine. The presence of unsapon. matter resulted in coarse emulsions; this happened in all the tests. An actual sizing expt., with as high as 50% unsapon. matter in the rosin size, showed that unsapon. matter had no effect on the sizing. The sapon. no. is not recommended as the test by which rosin should be judged as to its sizing quality; rather, the color should be used as the quality test. J. L. PARSONS

**Nitrocellulose composition.** H. T. CLARK. U. S. 1,444,333, Feb. 6. Butyl, isobutyl or amyl salicylate is used as a solvent in nitrocellulose compns. adapted for manuf. of films or varnishes together with acetone, MeOH, fusel oil or other solvents.

**Cellulose ether composition.** S. J. CARROLL. U. S. 1,444,331, Feb. 6. Phenyl-propyl alc. is used with cellulose ethyl ether as a solvent together with MeOH, EtOH, or other alcs. in the production of films. Cf. C. A. 16, 3758; 17, 467.

**Cellulose ether composition.** W. R. WEBB. U. S. 1,444,406, Feb. 6. Ethylene

chlorohydrin is used as a solvent with cellulose ethyl ether in compns. adapted for films, varnishes or molded articles together with MeOH or other solvents. Cf. *C. A.* 17, 467.

**Sulfite waste-liquor emulsions for core binders, etc.** K. P. McELROY. U. S. 1,444,844, Feb. 13. A small amt. of soda sludge from petroleum refining is used with waste sulfite liquor to emulsify linseed oil or other oils for core, road or briquet binders.

**Hardening linings of sulfite pulp digesters.** C. H. JONSSON. U. S. 1,444,467, Feb. 6. Fresh linings of acid-proof bricks and mortar in sulfite pulp digesters are hardened by exposure to gaseous  $\text{SO}_2$ .

**Oiled paper.** S. SPARKS. U. S. 1,444,217, Feb. 6. Oil is applied to portions only of a strip of paper and the paper is then passed over rollers and wound to permit diffusion and penetration of the oil.

**Rendering paper transparent.** O. POEPEL. U. S. 1,444,082, Feb. 6. Paper for window envelopes is coated with a lacquer at certain portions and then passed through a heated chamber where the heating and motion of the paper cause impregnation with the lacquer and render the paper transparent.

**Sizing paper stock.** J. A. DeCEW. U. S. 1,444,956, Feb. 13. Filling material such as clay for loaded paper stock, in aq. suspension, is treated with a dil. colloidal aq. soln. of a free rosin size and after thorough mixing of the ingredients they are added to paper stock in a heating engine. U. S. 1,444,957 relates to a heating engine construction.

**Sedimentation of fine paper pulp.** L. M. BOOTH. U. S. 1,443,454, Jan. 30. The solid particles in "white water" from Fourdrinier paper machine screens are recovered by adding reagents such as a mixt. of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Na}_2\text{CO}_3$  to assist in coagulation or sedimentation. Cf. *C. A.* 17, 1328.

**Operating Fourdrinier machines.** P. K. BAIRD. U. S. 1,442,848, Jan. 23. The atm. directly over the apron of a Fourdrinier paper-making machine is electrostatically charged, in order to eliminate foam or froth.

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

**Making fulminate of mercury.** R. K. BREWSTER. *Hercules Mixer* 4, 247-50 (1922).—An admirably illustrated account of the methods followed at the plant at Prescott, Ont., Can., which has a capacity for producing about 5000 lbs. daily, showing the technic of the operations.

CHARLES E. MUNROE

**Study of nitrocellulose.** E. C. BINGHAM AND W. L. HYDEN. *J. Frank. Inst.* 194, 731-40 (1922).—To ascertain whether the fluidity of nitrocellulose solns. is a linear function of the concn. only, or is influenced by the shearing stress, the mobility of solns. of nitrocellulose (N.C.) (12.11% N) in  $\text{Me}_2\text{CO}$  was detd., at various temps., and concns. and with varying shearing stresses, by the viscosimeter. These detns. showed a steady increase in fluidity with the pressure and that efflux was a linear function of the shearing stress. By extrapolating the shearing stress to its value when the efflux is zero the friction or "yield value" is obtained. *Yield value* is defined as the shearing stress at the wall of the tube necessary to start the flow, and it increases with increasing concn. and decreasing temp. On plotting this against temp. for N.C. (7.708% N) soln. in  $\text{Me}_2\text{CO}$  a sharp transition temp. is indicated at 43° when the "yield value" becomes zero and the material loses its plastic character to become a viscous liquid. The probability is that this transition temp. is independent of the concn. The mobility of N.C. dispersions is characterized by the great depression produced by very small percentages of the solid,

a 1% soln. having 20%, and an 8% soln. 0.1% the mobility of the pure solvent. This is one of the most noteworthy distinctions between the polar and non-polar type of colloid. The mobility increases with the temp. in a nearly linear manner.

CHARLES E. MUNROE

**The analysis of TNT-tetryl mixtures.** C. A. TAYLOR AND WM. H. RINKENBACH. *Ind. Eng. Chem.* **15**, 280-1 (1923).—The analysis of mixts. of TNT and tetryl occurring in detonating fuse and elsewhere in the explosive art has been effected by detns. of the N content by the Dumas method and calcg. the relative percentages of the components present from this datum. This process, being slow, tedious and subject to error T. and R. have, from their studies of the solubilities of TNT and of tetryl in various org. solvents and of the f.-p. curve of a binary system of these components (C. A. **17**, 880), worked out a method of analysis based on the relative solubilities of these substances in  $\text{CCl}_4$  at  $0^\circ$ , which is easily and rapidly carried out with their wagon-pipet or by an extemporized app.; there is given an accuracy of results within 2%. CHARLES E. MUNROE

**Collection and examination of explosive dusts in air.** L. J. TROSTEL AND H. W. FREVERT. *Ind. Eng. Chem.* **15**, 232-6 (1923).—Paper thimbles, contg. well fluffed-out cotton-wool to act as a support for the dust and prevent this from clogging the pores of the paper, were attached to a portable, calibrated, hand pump, or an elec. driven blower, equipped with Venturi meter, and a manometer; a measured vol. of air was passed through the thimble; and the increase in wt. of the latter noted. The optical filtering efficiency found against tobacco smoke was 46.2%, and against air-floated  $\text{SiO}_2$  dust 100%, after an average initial lag of 37 secs. The gravimetric filtering efficiency found against starch dust was 99.5%. Data of value in dust explosion studies were obtained (a) solids per cu. ft. of air, (b) particle size and compn., (c) in heavy samples, the "relative flammability."

CHARLES E. MUNROE

**Spontaneous ignition of benzine.** "V." *Schweiz. Apoth. Ztg.* **60**, 489-91; A. BRUN. *Ibid* **60**, 566 (1922).—The spontaneous ignition (observed during a thunder-storm) of a jet of dry benzine upon striking a filter paper is probably an elec. phenomenon, paper and benzine being oppositely charged. B. points out the danger in pouring anhydrous benzene, petr. ether and  $\text{Et}_2\text{O}$  from glass to glass; under these conditions, sparks are frequently seen in the dark, mostly insufficient to cause ignition.

S. WALDBOTT

**Fumes encountered in mining operations and handling of explosives.** J. BARAB. Hercules Powder Co. mimeographed, 43 pp. July 10, 1922.—Such progress has been made in the development of explosives producing on explosion the min. amt. of poisonous gases while giving the desired explosive effect that complaints of fumes from explosives and of mine-gas poisoning are becoming comparatively rare. Because of their infrequent occurrence the physician or other person entrusted with the sufferer is usually ignorant of the necessary action to take and the proper treatment to be given. B. has therefore brought together the results of a careful survey of available information. There is given in tables the kind and quantities of the gaseous products of combustion of many varieties of explosives, the effect of paraffined paper wrappers, and the effect on the atms. of different classes of explosives fired in zinc and in limestone mines, together with much other useful data. Examples from experience of poisoning are given, and a review of the methods of treatment to be followed in such instances. C. E. M.

**Report on fire in Manufacturers' Transit Co.'s warehouse, N. Y.** N. Y. Board of Fire Underwriters, *Bureau of Surveys*, 4 pp., 9 plates. No date.—The fire and explosion occurred July 18, 1922 in a 6-story and basement fireproof building of steel construction 10-14 Jane St. and 245-251 W. 12th St., N. Y. City, probably due to friction from a hook or other source igniting a case of Mg powder in the elevator shaft where approx. 18 cases, each  $18 \times 18 \times 30$  inches, were being removed from the elevator



to the sidewalk, about 6 of which are said to have been removed from the elevator at the time the fire started. Several minor explosions, or puffs, accompanied by intensely white flame, occurred in the elevator and the street which were increased in intensity when water was thrown on the cases. After the fire had been burning 20 mins., coincidentally with turning the stream from the hose into the elevator shaft a violent explosion occurred which blew out the west wall of the shaft. The explosion is attributed to  $H_2$  from reaction of the  $Mg + H_2O$ , forming an explosive mixt. and also the powdered  $Mg$  stirred up by the force of the stream projected against it forming an explosive mixt. with air in the shaft. One was killed and 20 were injured as a result of the explosion. On several floors of the warehouse news print paper was stored and this expanded so greatly when wet as to push down and badly bulge all 4 walls of the building. Such material should be so stored as to allow of 20% expansion in any direction.

CHARLES E. MUNROE

**Practical method for preventing explosions due to accumulations of static electricity.** H. I. JONES. *Chem. Met. Eng.* 27, 924(1922).—J. holds that most "mill dust," gasoline "tumbler" and powder mill explosions are caused by sparks of static electricity whose formation may be prevented by ionizing the air, thus "draining-off" the static as fast as produced. The air may thus be protectively ionized by ultra-violet light, by X-rays, by radioactive substances or any other means that will cause the emission of electrons in sufficient concn. J. found a tube of the Crookes' type best but as glasses vary in permeability to electrons a special glass is now being sought from which to construct such tubes for factory use.

CHARLES E. MUNROE

**Explosions in liquid-air plants.** Discussion. *Chemistry & Industry* 42, 127-8R (1923).—Discussion of the paper of Fyleman (*C. A.* 17, 1147), who attributed such explosions to  $C_2H_2$  produced by oxidation of the oil used to lubricate valves and other parts. W. R. ORMANDY stated this evidently has a bearing on the mysterious explosions which occur at times in the air compressors of Diesel engines carrying air at pressures of 1000-1200 lbs. per sq. in., the danger of which had been reduced by substituting steel for Cu coils to bring the air from the compressor to the engine. J. A. HARKER emphasized the importance of keeping a liquid-air plant well away from any place where  $C_2H_2$  was being used. This was difficult during the war at N-fixation plants. At Muscle Shoals, conduits extending, one  $1/2$  mile north, the other  $1/2$  mile south, were constructed to take air uncontaminated with  $C_2H_2$  into the liquid-air plant. FYLEMAN said even if there were but traces of  $C_2H_2$  this would collect in the O in the solid state. The reason why liquid O explodes so violently is that its heat of vaporization is but 50 so that the total heat of the C or  $C_2H_2$  is diminished by this quite small amt. and the results are startling.

CHARLES E. MUNROE

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Action of ammonium nitrate and of aqueous ammonia on copper (BASSETT, DURRANT) 6.

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**Explosive containing ammonium nitrate.** W. M. DEHN. U. S. 1,444,594, Feb. 6. Explosives are prepd. by heating wood meal or other plant tissues with  $H_2O$  and  $NH_4NO_3$  and evapng. the  $H_2O$ .

## 25—DYES AND TEXTILE CHEMISTRY

I. A. OLNEY

**Synthesis of substantive azo dyes derived from naphthalene.** N. N. VOROSHOV. *Bull. inst. Polyt. Ivanovo-Voznesensk* 4, 95-109(1921).—Insofar as the formation of azo coloring matters of substantive character is concerned, the analogs of benzidine in the naphthalene series are, not the bimol. naphthidines, but the unimol. naphthylene-diamines with the two amino groups in the 1,5-, 1,4-, 2,6-, and 1,6-positions. The scale of colors given by these coloring matters approximates to that obtained with the corresponding compds. of the benzidine series. J. C. S.

**Changes of indigo dyeings in light and during laundering.** R. HALLER. *Textilber.* 3, 433-4(1922).—Pieces of the same structure and wt. which had been bowked in the usual way were dyed in a 10% soln. of 20% indigo paste. Six common types of vats were used. After dyeing (light shade), the pieces were aged thoroughly, washed, scoured, washed again and dried. The colors were analyzed on Ostwald's scale and by the app. recommended by Ostwald. The changes observed after 2 and 3 months' exposure are shown in a table. Decreases in the full color, blue, varied from 1 to 15% absolute for the longer period. The relative % changes are 9-75. Poorest results are those in which a  $\text{Zn-Ca(OH)}_2$  vat was used, while the best results were those of the  $\text{Na}_2\text{S}_2\text{O}_4$ -NaOH and the  $\text{FeSO}_4$ -NaOH vats. By dialysis, it is shown that there is no direct relationship between light-fastness and size of the indigo-white particles in the vat. Changes in % of white, black, and pure (full) color of dyeings washed with 10 g. soap and 10 g.  $\text{Na}_2\text{CO}_3$  per l. for one hr. at the b. p. are tabulated. The same order of fastness is not found as in the light series, excepting for the first and last positions. W. F. FARAGHER

**Review of recent progress in the chemical technology of the textile industries.** A. CHAPLET. *Rev. chim. ind.* 31, 25-30(1922). A. P.-C.

**The importance of oils and fats for the textile industry.** F. HÖCHTLEN. *Textilber.* 3, 401-4, 422-4(1922).—An address, reviewing the uses of mineral oils (as textile oils), and of fats, fatty oils, and products prepd. from them. W. F. FARAGHER

**Silk.** F. URZ. *Chem.-Ztg.* 47, 36-7(1923).—The av. compn. of raw silk may be given as  $\text{H}_2\text{O}$  11, bast 23, mineral matter 1, fibroin or silk 65%. The % of silk bast is detd. by boiling a sample (of known  $\text{H}_2\text{O}$  content) with 600 cc. of a 0.75% soln. of olive oil soap for 70 min. The sample is washed 3 times with 500 cc.  $\text{H}_2\text{O}$ , dried at 105-20°, and weighed. In this manner the silk bast is extd. The silk content is calcd. from the N value. One part N corresponds to 5.455 parts water-free silk. A method is outlined for the detn. of N. C. T. WHITE

**The influence of length of time of bleaching on the strength of cotton fabrics.** II. P. HEERMANN AND H. FREDERKING. *Textilber.* 3, 465-6(1922); cf. C. A. 16, 2415, 2416.—Repeated bleaching of test pieces was carried out with a soln. contg. 0.5 g. available Cl per l. at 20°. The time of each test was 6.25 hrs. (to complete the series 0.25 hr., 1.25 hrs., and 6.25 hrs., the times being in the proportion 1:5:25). After 50 treatments the pieces had breaking strengths averaging 53.3% of the original, elasticities averaging 85% of the original, and weights/sq. in. 94.7% of the original. Relatively the greatest harmful action takes place during the first 15 min. of any treatment. After about the first 30 min. of a treatment, the weakening of the fibers is directly proportional to the time. By comparing the 1.25 hr. series with the 6.25 hr. series, it is seen that increasing the time 5-fold increases the corrosive action 3.5-fold. W. F. FARAGHER

**Preliminary note on the destruction of cotton hair by microorganisms.** H. J. DENHAM. *J. Text. Inst.* 13, 240-8(1922); cf. FLEMING AND THAYSEN, C. A. 15, 3536;

16, 3501.—The material used was "country damaged" cotton, mildewed cloth, cotton milldriving rope, Sea Island cotton stained by boll weevil, seed cotton especially Indian types and bolls of upland cotton attacked by *Fusarium* sp. Single hairs were mounted in liquid paraffin B.P. and examd. Cotton hairs are liable to attack at several points, which in the order of their vulnerability are: broken ends of the hair and cracks reaching to the lumen, abrasions, shallow cracks and pits, the normal surface of the cuticle. The central canal is by far the most commonly affected probably on account of the N substance present. The invasion of saprophytic forms is the rule. Other groups involve organisms living in the wall layers or on the surface are probably the cellulose-destroying types. All 3 types of growth merge into or overlap each other. The results are shown in 37 photomicrographs. Serious damage may exist in cotton before it can be detected by the usual tests. L. W. RIGGS

**The decomposition of bast fibers.** VI. P. KRAIS, K. BILTZ, AND A. HOPFFE. *Z. angew. Chem.* 35, 713-4 (1922); cf. *C. A.* 15, 1078.—The retting of bast fibers has been carried out in distd.  $H_2O$ , 0.8%  $NaHCO_3$  soln., and with the addn. of certain dyes such as Auramine O, Chrysodine, and Crystal Violet, in dil. soln. Results indicate that in an 0.8%  $NaHCO_3$  soln. bacterial growth is most favorable and that retting may be carried out in the shortest time. However, an 0.8%  $NaHCO_3$  contg. Auramine O in a diln. of 1:5000 gives a better product than the  $NaHCO_3$  soln. alone. Dil. soln. of Chrysodine and Crystal Violet are not favorable to bacterial growth. C. T. WHITE

Classifying and measuring color (TENNEN) 2. Indigo group II. A new vat dye from indigo and malonic ester (POSNER, PYL) 10.

**Dyes from naphthalenebisoxathiophenes and similar compounds.** M. P. SCHMIDT and H. ROESE. *U. S.* 1,444,277, Feb. 6. Naphthalene-2,6-dithioglycolic acid on treatment with chlorosulfonic acid and cooling forms naphthalene-2,1,5,6-bisoxathiophene and yields a dye forming a violet-red vat from which cotton is dyed fast green. Naphthalene-1,5-dithioglycolic acid yields a dye giving a muddy blue-violet on cotton. 1-Chloronaphthalene-3,8-dithioglycolic acid yields a brown-violet dye. By condensing equimol. proportions of the bisoxathiophene obtained from naphthalene-2,6-dithioglycolic acid and chloroisatin a brown-black vat dye is obtained giving brown-olive on saponifying. 1 or 2 mol. proportions of chloroisatin with the naphthalene bisoxathiophene from 1-chloronaphthalene-3,8-dithioglycolic acid yields a brown vat dye. Bromoisatin also may be used with similar effects instead of chloroisatin. The naphthalenebisthioglycolic acids may be used directly as starting materials and condensed with chlorosulfonic acid during the process.

**Diaminodinaphthyl- and dinaphthacarbazole-sulfonic acids.** KALLE & Co., AKT.-GES. Ger. 343,149. 1,1'- or 2,2'-Azonaphthalenesulfonic acids are treated with acid or alk. reducing agents. E. g., 1,1'-azonaphthalene-5,5'-disulfonic acid by reduction with tin and HCl gives 1,1'-diamino-2',2'-dinaphthyl-5,5'-disulfonic acid. It forms colorless needles and gives a yellow diazo compd. with  $HNO_2$ . By the action of Na amalgam in weak alk. soln. 1,1'-diamino-2,2'-dinaphthyl is formed, which by heating with HCl readily gives dinaphthaimine [di- $\alpha,\beta$ -naphthacarbazole]. On heating the acid with HCl at  $140^\circ$ ,  $NH_3$  is eliminated. 1,1'-Azonaphthalene-4,4'-disulfonic acid gives, by reduction with a hot alk.  $Na_2S_2O_4$ , an acid crystg. in fine needles which cannot be diazotized, and on heating with mineral acids at  $130^\circ$  gives di- $\alpha,\beta$ -naphthacarbazole. It is therefore supposed to be di- $\alpha,\beta$ -naphthacarbazole-5,8-disulfonic acid. The reduction product from 2,2'-azonaphthalene-7,7'-disulfonic acid crysts. in compact, colorless needles and gives with  $HNO_2$  a yellow tetraazo compd. On heating with mineral acids at  $130^\circ$ , the 2,2'-diamino-1,1'-dinaphthyl-7,7'-disulfonic acid gives di- $\beta,\alpha$ -naph-

thacarbazole with intermediate formation of di- $\beta$ , $\alpha$ -naphthacarbazole-2,12-disulfonic acid. The products are used in the prepn. of coloring matters. J. C. S.

**Dyeing.** TETSUJI IMAI. Japan. 40,089, Sept. 28, 1921. Shaded patterns are dyed on a cloth by the following process. Cloth is treated with an oxidizable dyestuff, such as methylene blue, etc. It is then painted with a mixt. of 100 cc. of 20%  $H_2Cr_2O_7$ , 20 cc. of 10%  $NaClO_2$ , 10 cc. of 10%  $K_2Fe(CN)_6$ , and 20 cc. of 10% gelatin soln., neutralized with  $NH_4OH$  in a dark chamber. After drying, it is exposed to sunlight through glass or other transparent or semi-transparent substance drawn with suitable patterns, washed with  $H_2O$ , immersed in a mixt. of 2 cc. of concd.  $H_2SO_4$ , 2 g. oxalic acid and 1 l.  $H_2O$ , washed with  $H_2O$ , treated with 1% warm Marseilles soap soln., washed with  $H_2O$ , dyed with mordant dyes, such as alizarin blue, etc., washed with  $H_2O$ , and dried.

**Selective dyeing.** TOKUSABURŌ HORIIE and KYŪTA KUBOTA. Japan. 40,076, Sept. 22, 1921. Patterns are printed on a cloth with a mixt. of 100 parts naphtha soln. of Al soap and 35 parts powdered talc. After drying, it is dyed, printed parts being protected from coloring. The paste forms resistant and flexible films and can be removed by immersing it in naphtha.

**Dyeing variegated colors.** H. T. FLEISHER. U. S. 1,444,786, Feb. 13. Hosiery is knitted from yarn composed of artificial silk thread twisted with cotton or other strong fiber, the thread is moistened during knitting and is then treated with a dye having a different action on the different threads.

**Artificial silk.** E. BRONNERT. Can. 227,876, Jan. 9, 1923. In the manuf. of threads from viscose glucose is added to the  $H_2SO_4$  bath to prevent the parchmentizing of the thread. Cf. C. A. 16,1158.

**Cotton-like material from straw.** YŌKICHI SHIMOMURA and TŌZŌ ARIMORI. Japan. 40,074, Sept. 22, 1921. Crushed straw is boiled for 1-1.5 hrs. with soap soln. contg. bran, washed with  $H_2O$ , immersed in a dil. soln. of rice-bran oil contg. alc., bleached with bleaching powder, treated with  $H_2O$  contg. cottonseed oil, dried and loosened mechanically.

**Material for spinning.** GONZABURŌ ENDŌ. Japan. 40,008, Sept. 20, 1921. Hemp or like material is boiled with dil. alk. soln., immersed in a mixt. of 180 l. of satd. soln. of  $Ca(OH)_2$  and 1 lb. of Turkey red oil, then sepd. from the soln. and dried in the air. Or after it is treated with  $Ca(OH)_2$  soln., it is once more immersed in a soln. of  $Na_2CO_3$  (3 lb.) in 180 l. of  $H_2O$ , washed with  $H_2O$  and dried. These treatments roughen the surface of the fiber.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

**Plumbiferous fog from white-lead paint.** HYRMAN. *Bull. acad. roy. med. Belg.* [5] 2, 407-15(1922).—A layer of varnish or paint composed of linseed oil and turpentine, contg. white lead ejects plumbiferous particles. This was shown by placing above such a layer a disk of paper impregnated with  $H_2S$  soln. Small black spots, due to formation of  $PbS$ , soon became visible on the paper. Air drawn through a flask coated with the paint gives a strong reaction with  $H_2S$ . The reaction disappears, however, if the air is drawn through cotton-wool which keeps back the particles. The reaction cannot be caused, therefore, by plumbiferous gases or vapors. From the size of the distinct black spots on the  $H_2S$  paper the diam. of the particles is estd. as less than  $30 \mu$ . Such small particles must sink so slowly—as can be calcd. from the law of Stokes—that they are practically afloat in the air for a long time, thus giving rise to intoxications. Such particles can also be demonstrated to be present in rooms painted with white lead. The authors object to the statements of Armstrong and C. A. Klein

(*C. A.* 16, 1324) who deny the possibility of the existence of such particles. The filter-paper, used by the authors, contained no Cu, which possibly could give rise to errors.

R. BEUTNER

**The removal of old paint.** HUTIN. *Rev. chim. ind.* 31, 202-5(1922).—Various formulas for paint removers are given.

A. P.-C.

**Modern research on anti-fouling paints and a note on wood borers.** H. A. GARDNER. Paint Mfrs. Assoc. of U. S., *Circ.* No. 157, 35-72(Oct. 1922).—A brief summary of the work under way, history of the problem of prevention of fouling, and a list of U. S. patents on anti-fouling compns. The present Navy plan of research includes a systematic chemicoxicological investigation in conjunction with a study of the life habits and methods of attachment of barnacles. A preliminary report by A. W. Bray on *barnacles* of the *balanus* species is given. Increase of skin friction of the keels of vessels which have not yet become fouled with barnacles and grasses is probably due to a bacterial slime which builds itself up on the paint film. Measurements of this frictional resistance, its effect on coal consumption, loss of speed, etc., are being made. Formulas are given of a very large no. of anti-fouling paints which are being tried out at the various Navy yards. Study of the protection of wood piling from *Teredo wood borers* is being made. In some previous tests the use of an alk. Cu soln. gave excellent results. A bibliography on marine borers is given. Illus.

F. A. WERTZ

**The use of furfural as a paint and varnish remover.** H. A. GARDNER. Paint Mfrs. Assoc. of U. S., *Circ.* No. 171, 140-7(Feb. 1923).—Furfural alone or mixed with 20% of solvent naphtha is an effective paint and varnish remover. It has the advantage over most removers that it is less fire hazardous, evaps. more slowly, is less harsh on the skin, and leaves the surface free from wax and ready for subsequent painting. For use on vertical surfaces it may be thickened. Review of the manuf. of furfural, bibliography, and patents involving its use, are given. Illus.

F. A. WERTZ

**Factors governing paint consistency.** HENRY GREEN. *Ind. Eng. Chem.* 15, 122-6(1923).—The factors on which consistency of a paint depends are those which govern yield value and mobility, that is the viscosity of the vehicle, the pigment-vehicle ratio, the force of flocculation in the pigment-vehicle system, and the particle size of the pigment. Yield value is due principally to the force of flocculation which in turn is dependent on the degree of wetting of pigment by the vehicle. The effect of deflocculation on yield values and mobility of various pigment paints are detd. with a plastometer and tabulated. The finer the pigment particle, the greater the force of flocculation. Flocculation decreases the mobility of a paint. The thinning of paints shortly after application or while still in the container is probably due to an increase in wetting power of the vehicle through absorption of O most likely from the surface of the pigment itself.

F. A. WERTZ

**An experimental drying-time tester (for varnishes).** H. A. GARDNER. Paint Mfrs. Assoc. of U. S., *Circ.* No. 167, 121-7(Feb. 1923).—The tester consists of a clock-operated drum which winds on to itself a blank moving picture film coated with the varnish, and a strip of tissue paper. The paper strip is brought into contact with the varnish film just as it is drawn on to the drum. The drying time is measured to the point where the paper ceases to adhere or becomes stained by the varnish film. Illus.

F. A. WERTZ

**The nature of chrome yellow.** JEROSLAV MILBAUER AND KAMIL KOHN. *Chem.-Zig.* 46, 1145-8(1922).—A discussion of the theory of the fractional pptn. of  $\text{PbSO}_4$  and  $\text{PbCrO}_4$  involved in the manuf. of lemon chrome yellow, and tabulation of results of the detailed study of the sp. case of a mixed soln.  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$  pptd. by  $\text{Pb}(\text{NO}_3)_2$  at various concns. at  $20^\circ$ . (Cf. *C. A.* 11, 554.) The equil. const.  $\text{K}_2\text{CrO}_4/\text{K}_2\text{SO}_4$  at  $20^\circ = 0.000277$ ; a more exact detn. of the const. was impossible owing to adsorption

phenomena. The extreme rapidity of the reaction, and the rapid decrease in the amt. of  $\text{PbSO}_4$  in the ppt. are notable. A similar study of the pptn. of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$  with  $\text{PbOAc}$  lead to less accurate results because of the soly. of  $\text{PbSO}_4$  in  $\text{KOAc}$ . The presence in the soln. of  $\text{KNO}_3$  increases the soly. of  $\text{PbSO}_4$  which in the presence of  $\text{K}_2\text{CrO}_4$  is subsequently pptd. as colloidal  $\text{PbCrO}_4$ . The compn. of the ppt. is independent of the quantity of the precipitant, but is independent only on the relation of  $\text{CrO}_4^{--}:\text{SO}_4^{--}$  in the soln. This makes conclusive the theory that attributes the properties of chrome yellows to formation of double salts (sulfochromates) and explains why it is not arbitrary which salts of  $\text{H}_2\text{SO}_4$  or  $\text{H}_2\text{CrO}_4$  are used to obtain a certain shade of chrome yellow, since dissociation of various salts will alter the relation  $\text{CrO}_4^{--}:\text{SO}_4^{--}$ . The various older theories on the formation of chrome yellow are discussed. The darkening of chrome yellow is usually attributed to hydrolysis of the  $\text{PbCrO}_4$  with subsequent formation of red basic chromate, but no satisfactory explanation has been given as to why  $\text{PbSO}_4$  reduces hydrolysis. This should be correctly attributed to formation of isomorphous mixts. and solid solns. of  $\text{PbCrO}_4$ , as shown by microscopic studies of the crystals and of the action of various solvents on them. Since  $\text{PbSO}_4$  has a greater tendency to ppt. in cryst. form from dil. solns., it is necessary for the production of lemon chrome yellows, to use very dil. solns. and to ppt. with continual stirring so as to induce formation of a max. transformation of the usually amorphous  $\text{PbCrO}_4$  into the isomeric cryst. form, and a max. degree of solid soln.

F. A. WERTZ

**Hiding power of white pigments.** R. L. HALLETT. *Proc. Am. Soc. Testing Materials* 22, II, 523-31(1923).—The hiding power of a paint coat is a geometric function of the thickness, so that complete hiding is theoretically obtained only by a film of infinite thickness. This is proven by coating black striped panels at the same spreading rate with paints contg. the same vol. of different white pigments. The thickness of each paint required to give apparent complete hiding was measured with the cryptometer, and the % of hiding of the black stripe on each panel was measured with the hidimeter (*C. A.* 14, 2863; 15, 1081). The actual hiding readings on the panels agree very closely with the hiding calcd. from cryptometer readings by means of a formula developed. Additional confirmation that hiding power is a geometric function of paint film thickness was obtained by measurements on panels to which paint had been applied at such a rate that the thickness of film and the amount of pigment on the panels varied at a constant rate. Tinting power expts., made by rubbing up white pigments with lampblack show that the hiding and tinting powers are direct measures of each other. Results are tabulated and plotted.

F. A. WERTZ

**The action of light on paint materials. V. Causes and elimination of the non-sunproofness of lithopone.** A. EIBNER. *Chem.-Ztg.* 47, 13-6(1923).—A brief review of the causes heretofore ascribed to the darkening of lithopone by light, and of the effect of light on pigments in general (*C. A.* 5, 3920). Analyses of all German lithopones showed Cd, Mn, Fe, Ni, Co, Pb, and in one case Th. Cl is not the cause of non-light-proof lithopones, but it decreases lightproofness by combining with heavy metal impurities to form light sensitive sulfochlorides. The discoloration of lithopones in light is strictly a chem. reaction caused by the phosphorescence of the calcined  $\text{ZnS}$  in actinic illumination, which in turn catalyzes the formation of colored sulfides of the heavy metal impurities. Bleaching of a light discolored lithopone occurs through oxidation of the heavy metal sulfides. Absolutely lightproof lithopones can be made if the original Zn solns. are purified by removal of Fe, Mn, Pb, Cd, and As with  $\text{NH}_4\text{OH}$ , and then pptg. all traces of Cu, Th, Ni, and Co through addn. of metallic Zn and heating for 12 hrs.

F. A. WERTZ

**Report of Sub-Committee IX (Com. D-1) on varnish.** E. J. COLE, et al. *Proc. Am. Soc. Testing Materials* 22 I, 375-81(1922).—Four varnishes of known compn,

and manuf. were tested for elasticity by the kauri reduction test (*C. A.* 13, 664), drying time, effect of hot and cold  $H_2O$  on the film, etc. Details of the tests are given, and reports of the members are tabulated.

F. A. WERTZ

**Report of Sub-Committee III (of Com. D.-1) on testing of paint vehicles.** H. A. GARDNER, *et al.* *Proc. Am. Soc. Testing Materials* 22, 1, 367-73(1922).—Results of cooperative analyses on samples of *chia*, *rubber-seed*, *sunflower-seed*, and *tung* oils are tabulated. These indicate that the Wijs method for detg. I nos. gives accurate results on tung oil, being about 2 points lower than the I nos. by the Hübl method. The lime treatment of tung oils (*C. A.* 16, 768) before the heat test should be omitted. This test may be applied if the purity of the oil is under suspicion, but tung oil of suitable quality for the varnish industry should fall within the specification limits on the heat test, without neutralizing their acidity with lime.

F. A. WERTZ

**Report of Sub-Committee XXIII (of Com. D.-1) on anti-fouling paints.** A. M. MUCKENFUSS, *et al.* *Proc. Am. Soc. Testing Materials* 22, 1, 394-415(1922).—Details of test panels of anti-corrosive and anti-fouling paints are given, and results of inspections tabulated and photographed. Cu compds. gave excellent anti-fouling properties in Raritan Bay, N. J., but were not as satisfactory as the Hg compds. at Charleston, S. C. Only these 2 poisons will be used in the further tests of the committee.

F. A. WERTZ

**Report on special tung oils.** H. A. GARDNER AND W. P. YARNALL. Paint Mfrs. Assoc. of U. S., *Circ.* No. 160, 96-8(Dec. 1922); cf. *C. A.* 16, 841.—Five samples of tung oil produced by a modern process at Shanghai were very high grade and passed every requirement of the A.S.T.M. specifications excepting that the  $d_{15.5}^{15.5}$  of one was 0.9444. Results are tabulated.

F. A. WERTZ

**Rubber latex in the paint industry.** H. A. GARDNER. Paint Mfrs. Assoc. of U. S., *Circ.* No. 170, 134-9(Feb. 1923).—A spread out film of rubber latex forms an opaque white surface which on evapn. develops into a clear transparent rubber film of firm surface. This suggests latex as a paint vehicle, but the addn. of most pigments as well as linseed oil, mineral spirits, etc., causes immediate coagulation and pptn. of the rubber, probably owing to disturbance of the equil. in the latex emulsion. A very few pigments, such as silica, do not cause this coagulation and a system based on protective colloids has been worked out to overcome the coagulating effect of other pigments and paint liquids (details not given), which may make possible the use of latex in paints. A very brief historical review of the rubber industry is given. Illus.

F. A. WERTZ

**Microscopy of paint and rubber pigments.** HENRY GREEN. *Chem. Met. Eng.* 28, 53-7(1923).—The microscopy of pigments requires a distinctive technic. A properly made pigment mount must have proper particle d., correct proportion of largest and smallest particles, suitable dispersion, and all particles in the same plane; and the mount must be observed in illumination that is critical and centered, and the magnification and resolution must be adequate. 1500 diam. is an av. satisfactory magnification. *ZnO particles*, *Am. process*, are 0.4 to 0.6  $\mu$  in size and are hemamorphic hexagonal prisms with acicular tendency and readily forming twins, threelings, and fourlings. *French process ZnO particles* are 0.3 to 0.4  $\mu$ , less acicular and without twinning tendency. *Leaded ZnO* contains the basic Pb sulfate in solid soln.; this causes the crystals to become short and thick. Characteristics and av. particle size of other pigments are: *lithopone*, non-cryst., 0.3 to 0.4  $\mu$ ; sunproof varieties under the fluorescent microscope are dark; non-sunproof, beautifully fluorescent; the  $BaSO_4$  and  $ZnS$  show up as separate ingredients in ultra-violet photomicrographs. *Basic carbonate white lead*: well defined hexagonal particles, 0.75 to 2.0  $\mu$ . *Basic sulfate white lead*: non-cryst., roundish particles, 0.65  $\mu$ . *Gas carbon black*: successfully photographed only in ultra-violet light, strong tendency to flocculate in all media, individual particle, 0.15  $\mu$ , appear grayish

or brownish, while those of lampblack, 0.3 to 0.4  $\mu$ , appear black. Inert pigments are easily recognized, av. particle size 5 to 10.0  $\mu$ . Microscopic methods are easily applied to pigment identification, particle size measurement, and the study of pigment flocculation. Cf. C. A. 16, 841-2.

F. A. WERTZ

**Printing inks and their manufacture.** MAURICE DE KEGHEL. *Rev. chim. ind.* 31, 45-54, 111-7, 143-7, 174-6, 232-8, 259-65(1922); et seq.—A general write-up.

A. P.-C.

**Naming and defining the fastness to light of printing inks.** MARTIN HARTMANN. *Farben-Ztg.* 28, 558-9(1923).—Printing inks may conveniently be divided into 5 grades based on their fastness to light, detd. by exposure according to the method of Kraus (*Z. angew. Chem.* 30, 298-303(1917)). Examples of various grades are given.

F. A. WERTZ

**Note on mineral spirits.** H. A. GARDNER. Paint Mfrs. Assoc. of U. S., *Circ.* No. 162, 102-5(Jan. 1923).—To test mineral spirits for freedom from darkening when used in thinning hot varnish bases, cover a strip of clean Cu, 0.5  $\times$  3 inches, in a test-tube, with the sample of thinner. Heat at its b. p. for 30 min.; any marked blackening of the Cu is cause for rejection. The character and amt. of residue on evapn. from a H<sub>2</sub>O-bath of 100 cc. of thinner in a Cu dish also give information on the selection of a proper thinner. Results on samples are tabulated. Illus.

F. A. WERTZ

**New researches on shellac and colophony.** HERMANN VOLLMANN. *Farben-Ztg.* 28, 486-7(1922); 562(1923).—A summary and review of the recent work of Harries and Nagel (*C. A.* 16, 3070), Tschirch (*Chem. Umschau* 29, 326(1922)), Aschan (*C. A.* 16, 3643), and others, on the constitution of shellac and the conifer resins.

F. A. W.

**Studies of the relationship between resinification and the constitution of chemical compounds. II. Description of a new method for the preparation of synthetic resins.** WALTHER HERZOG AND J. KREIDL. *Z. angew. Chem.* 35, 465-7(1922); *Oesterr. Chem. Ztg.* 26, 1-3(1923); cf. C. A. 16, 1671.—The preparation of a number of resins by the use of the resinophor group,  $-\text{CH}=\text{CH}-\text{CO}-$ , is described. The products are formed by polymerization. Resin from dibenzylideneacetone, prepd. by heating under CO<sub>2</sub> at 180° in 98% yield, is red-brown solid, m. 85-95°, easily sol. in organic solvents. When purified by dropping Et<sub>2</sub>O soln. into excess petr. ether, m. 170-185°. Crystalline tetrabromide m. 207-8°. Resin from dianisylideneacetone,  $(\text{MeO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH})_2\text{CO}$ , prepd. by heating at 220-5°, is a brittle red-brown mass, m. 70-100°. Resin from dicinnamylideneacetone,  $(\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}=\text{CH})_2\text{CO}$ , m. 130-45°; benzylidenecinn-


anilydeneacetone,  $(\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CO}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}_6\text{H}_5)_2$ , m. 115-20°; from

anisylidenecinnamylideneacetone,  $\text{MeO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CO}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{MeO}$ , m. 135-40°; from dipiperonylideneacetone,  $\text{CH}_2=\text{C}(\text{C}_6\text{H}_4\text{O})-\text{CH}=\text{CH}-\text{CO}-$

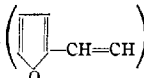
$\text{CH}=\text{CH}-\text{C}(\text{C}_6\text{H}_4\text{O})_2-\text{CH}_2$ , m. 155-70°; from benzylidenepiperonylideneacetone,

$\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CO}-\text{CH}=\text{CH}-\text{C}(\text{C}_6\text{H}_4\text{O})_2-\text{CH}_2$ , m. 70-80°; from piperonylidenecinn-



amylideneacetone,  m. 125-35°;

from furalcinnamylideneacetone,  m.

135-55°; and from difuralacetone,  CO, m. 55-75°. A discussion of

the mechanism of resinification is included.

J. B. BROWN

**Accuracy of methods for the determination of rosin (colophony) in several types of varnishes.** W. T. PEARCE. *Drugs, Oils and Paints* 38, 118(1922).—A brief review is given of previous work on the detn. of rosin, and results obtained on several varnishes by a modified McIlbeny method are tabulated. Saponify 5 g. of varnish with 100 cc. 0.5 N alc. KOH; evap., dissolve in 50 cc. abs. alc. and neutralize with 0.5 N abs. alc. AcOH. Add 50 cc. petr. ether, add H<sub>2</sub>O and allow to stand in an ice chest for 12 hrs. Then sep. the ether layer, wash, evap., and esterify the residue by the Wolf method. The amt. of rosin is calcd. from the acid no. of the rosin acids. Results on varnishes of known rosin content are unreliable.

F. A. WERTZ

**Examination of an interesting strain of flaxseed.** H. A. GARDNER. *Paint Mfrs. Assoc. of U. S., Circ. No. 166*, 119-20(Jan. 1923).—A particular strain of seed, propagated by Burbank and grown in Alberta, contains 46% oil, instead of the usual 40% or less, of I no. 189. The crop matures during a short growing season.

F. A. W.

**Classification and analysis of varnish resins.** P. C. HOLDT, H. A. GARDNER, AND P. E. JAMESON. *Paint Mfrs. Assoc. of U. S., Circ. No. 159*, 77-95(Nov. 1922).—A scheme for the classification and analysis of varnish resins is suggested, based on the relative proportions of resin acids and unsapon. matter which they contain. This method promises to give information which will show the possible value of unknown resins in varnish making. Definite methods of analysis are outlined, and compns. of various resins tabulated. On certain resins, a considerable difference was found between the direct and indirect acid nos. This is usually designated as ester value, but the authors believe the difference is due to aldehydes, and designate it as aldehyde no. A complete bibliography on varnish resins is given.

F. A. WERTZ

**Purchasing specifications for resins and shellac—a review of the question.** Wm. B. PARKER. *J. Oil & Colour Chem. Assoc.* 5, 197-258(1922).—A general discussion of the chem. and phys. tests and phys. characteristics which are adaptable to use in specifications for resins and shellac. Suggested specifications for 5 grades of shellac include general phys. characteristics and the following:

Grade.	Ash. (Max.)	I No.	(Häbl. 24 hrs.)	Acid No.	Sapon. No.	Petr. ether. Ext. max.	(8 hrs. min.)	Rosin (max.)
Pure Button	0.6%	8.0		66	225	3%	6%	0
Black Button	2.0%	14.		66	225	3%	10%	5%
Pure Lemon	0.7	7.5		60	200	3%	6%	0
Pure Orange	1.0	9.0		60	200	3%	8%	0
Stand. T. N.	1.5	14.0		66	225	3%	9%	3%

160 parts by wt. of any grade dissolved in 246 parts cold methylated spirits, d<sub>15.4</sub>, 0.8201, and allowed to stand for 12 hrs. shall yield a soln. of d<sub>15.4</sub> approx. 0.925. The soln. shall strain freely through a 60-mesh sieve and be free from undissolved particles. Speci-

fifications for New Zealand kauri, spirit-sol. Manilla copal and East Indian dammar resin grade the sizes of pieces according to wt. of av. pieces, and give limiting values to ash, acid no., sapon. no., and I no. (Hübl. 24 hrs.). The hardness of various resins detd. with a Shore scleroscope is tabulated. Discussion. F. A. WERTZ

**Investigation of some linseed oils.** H. A. GARDNER. Paint Mfrs. Assoc. of U. S., *Circ.* No. 158, 73-6 (Nov. 1922).—Forty samples of linseed oil from various parts of the East indicate that most of the oil available on the market is from S. Am. origin. Complete analytical results on the oils are tabulated together with drying time on white lead and lead-zinc paints made with the oils, of which exposure panels have been prepd. Oil extd. with benzene from flax meal that had been in freight transit for several weeks showed a very high acid no. probably due to enzymes and the action of moisture. Illus.

F. A. WERTZ

**Formation of resins by the evaporation of turpentine products in open vessels.** H. A. GARDNER. Paint Mfrs. Assoc. of U. S., *Circ.* No. 163, 106-8 (Jan. 1923).—The resinous residues obtained on evapn. of turpentine and pine oils in Cu dishes showed acid nos. of 3 to 17. Blowing air through freshly distd. turpentine and then evapg. increased the quantity of residue obtained. These resinous products are free from rosin and probably the result of oxidation and polymerization. Illus. F. A. WERTZ

**Laboratory experiments on converted pine spirits.** H. A. GARDNER, P. C. HOLDT, AND H. C. PARKS. Paint Mfrs. Assoc. of U. S., *Circ.* No. 164, 109-16 (Jan. 1923).—Converted pine spirits produced by processing the higher-boiling fractions of steam-distd. pine wood spirits were examd. for chem. properties, miscibility, solvent properties, evapn. rate, effect on viscosity of varnishes, etc. The product apparently contains substantial amts. of cymene or *p*-cymene and promises to be useful in the paint and varnish industry. F. A. WERTZ

**Formation and demolition of stick-lac.** A. TSCHIRCH. *Schweiz. Apoth. Ztg.* 60, 609-11 (1922).—The insect, attaching itself to the plant, elaborates in its body resin and wax with which it surrounds itself. Resin and wax contain aliphatic substances only. The red dyestuff formed in the body of the insect, probably by bacteria, belongs to the aromatic series. The chief products of successive extn. of stick-lac with  $H_2O$ ,  $EtOH$ , xylene,  $NaOH$ , are *laccic acid* (*L*) (*C. A.* 7, 3481); an acid resin contg.  $Et_2O$ -sol. volatile odoriferous cryst. matter, also golden yellow *erythrolaccin*  $C_{12}H_{10}O_3$  (T. and Farnier) related to emodin, and *aleuritic acid*,  $C_{16}H_{12}O_5$ , insol. in  $Et_2O$  (trihydroxypalmitic acid, Harries); wax, and a 3rd dye related to *L*, located in the hull of the insect.

S. WALDBOTT

**Measuring the hardness of resins.** CH. COFFIGNIER. *Rev. chim. ind.* 31, 9-13 (1922).—A large number of hardness measurements made by the method of C. A. 15, 2002 are given. Measurements were made with various loads, diams. of ball, lengths of time, and temps. A. P.-C.

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Determination of abietic acid and of rosin (SCHULZ, LANDA) 7.

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**Zinc sulfide.** A. HELLBRONNER and P. PIPERHAUT. U. S. 1,443,077, Jan. 23.  $ZnS$  adapted for use as a pigment is obtained by calcining  $ZnSO_4$  with sawdust or other carbonaceous material,  $MgSO_4$  and  $H_2SO_4$ , and leaching the product with dil.  $H_2SO_4$  to leave  $ZnS$ .

**Apparatus for calcining lithopone.** J. L. MITCHELL. Can. 228,195, Jan. 23, 1923.

**Mixed synthetic resins.** I. WEISBERG. U. S. 1,443,935, Jan. 30. Phenol-formaldehyde resins and glycerol-polybasic acid resins are mixed together to form elec. insulators or other articles of good strength, toughness, resistance to shock and which

can be readily hardened, or to form varnishes. Common solvents may be utilized for blending the resins and the usual fillers or modifying agents may be added.

**Synthetic resin mixtures.** L. WEISBERG. U. S. 1,443,936, Jan. 30. Resins of the class which may be derived from glycerol, phthalic anhydride and succinic, malic, tartaric, maleic or fumaric acid and which are of the nature of intermediate condensation products infusible and insol. in acetone ("class B" products) are treated with hot acetone, together with shellac or other resins, gums, fillers or coloring agents, to effect swelling of the synthetic resin and produce a blended moldable compn. The acetone is then distd. from the mixt.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

**Mafurra tallow, a product of the nuts of *Trichilia emetica*.** M. RINDL. *S. African J. Ind.* 5, 415-23 (1922).—Both the husk and the kernel of mafurra nuts from Portuguese East Africa furnish a solid fat, while an oil is obtained from the aril. The aril oil has the following characters:  $d_{40}^20$  0.931, acid value (as oleic acid) 8.9%, sapon. value 202.5, I value 66, sapon. value of acetylated oil 235. The oil congeals if kept for some time at about 5°. The consts. of the solid fat obtained from different sources vary so widely that it is certain that all the com. material is not derived from the same species of *Trichilia*. The kernal usually contains about 60% of fat, and the husk 25-35%. It has a high m. p., ranging usually from 35-45°, and yields 7-8% of its wt. of glycerol on sapon. It has a notably high acid value (40-50).

J. C. S.

**Stearic acid in the latex of *Ficus fulva*, Reinw.** A. J. ULTÉE. *Bull. Jard. bot. Buitenzorg* [iii] 5, 105-6 (1922).—The latex contains large quantities of a wax, which, on hydrolysis, yields stearic acid. There is but little rubber present. *Ficus elastica* latex contains much smaller quantities of a different wax.

J. C. S.

**Naphthenic acids.** J. DAVIDSOHN. *Seifensieder Ztg.* 50, 2-4, 26-7, 37-8 (1923).—Naphthenic acids are recovered from the alkali refining wastes of Russian kerosene oils. Their properties resemble those of coconut oil; they are slightly sol. in  $H_2O$ , volatile with steam, possess a neutralization no. of 262 and require only small amts. of alkali for sapon. The Na salt is less hydrolyzed than ordinary soaps, coloring phenolphthalein in an 18% soln. of alc. while other soaps require a 40% alc. The alkali of naphthenic acid soaps can be detd. by direct titration of the soap soln. with 0.5 *N* acid, with methyl orange. Charitschkov's qual. tests for naphthenic acid, the pear-odor of its Me or Et ester and the green color with Cu salts, were found to be unreliable and D. substituted a test of his own. The soap is dissolved in  $H_2O$ , and a 10%  $MgCl_2$  soln. is added in excess; the mixt. is then boiled and filtered. The filtrate is evapd. to a small bulk and a few drops of HCl are added; a white turbidity or ppt. indicates naphthenic acid. No quant. method for mixts. has thus far been worked out. Naphthenic acid attacks metals at room temp. after 3 mos. as follows, expressed in g. per 1 kg. of metal: Pb 6.10, Zn 4.68, Cu 0.56, Sn 0.18, Sb 0.11, Fe 0.08, and Al 0.0. It attacks  $PbO$ , forming a thick jelly in 24 hrs. The acid as well as its Na salt acts as an *antiseptic*. The Na soap requires more salt in salting out than coconut oil soap. By sulfonating naphthenic acid with fuming  $H_2SO_4$  only a moderate sulfonation takes place. Three formulas are given with directions for the production of a *lubricating grease*, with CO as hardening agent. A list is given of 15 Ger. patents on the production and utilization of naphthenic acid.

P. ESCHER

**Isomerism in fatty oils and its technical significance.** A. EIBNER. *Chem. Umschau Fette, Oele, Wachse u. Harze* 29, 309-13, 317-21 (1922).—The possibility of isomers in mono-, di-, and simple and mixed triglycerides, and the minor isomerism due to the

presence of an asymmetric C atom are discussed and Hahn's formula for calcg. the possible no. of glyceride isomers is given. Sixteen isomers of oleic acid are possible, depending on the position of the double C-bond, none belonging to the drying acids. Fourteen isomers of linolic acid are possible; the 9, 10- to 12, 13-isomers form drying films of the poppy-oil type (ether-sol., melting on heating and easily cracking). Chinese wood oil contains eleostearic acid with 2  $\text{CH}_2$  groups between its 2 double bonds; it is this position that accounts for the extraordinary drying quality of wood oil.  $\alpha$ -Eleostearic acid, m.  $48^\circ$ , is converted into the  $\beta$ -acid, m.  $72^\circ$ , by exposure to light in alc. soln. This phototropic property is unknown in other oils or acids. The clupanodonic acids are supposed to have only 1  $\text{CH}_2$  group between their several double bonds, but this supposition needs verification. Acids of the castor-oil group contain the hydroxy group OH and their graphic formulas  $\text{CH}_2(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}:\text{CH}(\text{CH}_2)_5\text{COOH}$  (Kraft) or  $\text{CH}_2(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_2\text{CH}:\text{CH}(\text{CH}_2)_5\text{COOH}$  (Lewkowitsch) suggest the existence of the unsatd. acid  $\text{CH}_2(\text{CH}_2)_5\text{CH}:\text{CHCH}:\text{CH}(\text{CH}_2)_5\text{COOH}$ , contg. two conjugated double bonds. No straight-chain acid with less than 18 C atoms is a drying acid, excepting isanic acid ( $\text{C}_{18}\text{H}_{30}\text{O}_2$ ) and the acids in chaulmoogra oil. The Bakelite procedure in making a film insol. and infusible appears analogous to the drying of linseed oil.

P. ESCHER

**The colorimetry of fatty oils.** H. HELLER. *Farben-Ztg.* **23**, 631-2(1923).—Neither the ash, nor the acid ext. of dark green vegetable oils showed any traces of Fe, but they gave positive tests for Mg. This is contrary to the anon. note (*Farben-Ztg.* **23**, 351(1922)) claiming that chlorophyll contains Fe, and is in accord with the findings of Willstätter (*C. A.* **8**, 3565).

F. A. WERTZ

**Oil splitting by castor-seed lipase.** J. J. STUBBOROUGH AND H. E. WATSON. *J. Indian Inst. Sci.* **5**, 119-32(1922).—Crude oils, such as coconut, mohua, ground nut, Hongay, Illipe, Maroti, cottonseed, and poppyseed, have been found to hydrolyze when stirred with crushed castor seeds and  $\text{H}_2\text{O}$  without the addn. of an activator. No such action takes place if the oil is first refined or if the castor seeds are not added. The hydrolysis is due to the volatile free fatty acids in the crude oil. The volatile acids removed from Illipe and Hongay oils by steam distn. and used as activators give results comparable with those obtained by equiv. amts. of  $\text{AcOH}$ . When  $\text{MnSO}_4$  is used as an accelerator the initial action is very slow if the oil has been refined by alkalis or even if it has been heated to  $100^\circ$  for  $1/2$  hr. The initial rate of hydrolysis may be increased by adding 3% of  $\text{AcOH}$  calcd. on the wt. of  $\text{MnSO}_4$  to the soln. of the latter; by adding some of the distillate obtained from steam distn. of the crude oil; by allowing the steamed oil to stand until its acid no. has increased; by grinding the crushed seed with  $\text{MnSO}_4$  soln. in part of the  $\text{H}_2\text{O}$  and allowing to stand for 12 to 18 hrs. before adding the oil and the rest of the  $\text{H}_2\text{O}$ . The activity of a lipase prepn. may be greatly reduced by passing into the oil steam which has been in contact with rubber tubing. An active enzyme prepn. can be made by grinding the seeds with 10 times their wt. of 1.6 g. per l. of  $\text{AcOH}$  and filtering. This enzyme requires no activator, but different prepn. vary as regards their activity. With Illipe and cottonseed oil it is not necessary to stir during the whole course of the hydrolysis. The rate of hydrolysis increases with the amt. of enzyme used; 5 to 6 g. of seed per 100 g. of oil gives good results. Addn. of  $1/2$  the enzyme at the beginning and the other  $1/2$  after 8 to 10 hrs. does not give such good results. Addition of enzyme equal to 5 g. of seed at the start and a further addn. equal to 2.5 g. of seed after 8 to 10 hrs. increases the rate of hydrolysis to a slight extent.

E. SCHERUBEL

**Installations for obtaining palm oil.** F. C. VAN HEURN. *Bull. mat. grasses inst. colonial Marseille* **1922**, 307-25.—A discussion of the various considerations which govern the installation of plants for producing palm oil.

E. SCHERUBEL

**Composition of cacao butter.** A. W. KNAPP. *Chem. Trade J.* **72**, 133-4 (1923).—The const. of cacao butter of 5 varieties of beans such as Grenada, Guayaquil (Machala), Guayaquil (Arriba), Accra Superior, Accra Inferior vary within narrow limits as follows: m. p. 33° to 34°, oleic acid 0.6 to 1.3%, I no. 34.3 to 36.1, sapon. no. 192-3, titer 48.9° to 50.1°, neutralization no. of fatty acids 198-9, butyro-refractometer at 40°, 45.5 to 46.3.

E. SCHERUBEL

**Animal waxes: their characteristics and sources.** CHAS. F. JURITZ. *S. African J. Ind.* **6**, 13-9 (1923).—This article discusses liquid waxes from the sperm and bottle nose whale, solid waxes such as wool and beeswax, also spermaceti and insect wax. The latter occurs in China. Wax from *Ceroplastas destructor* Newst. had  $d_{15}$  0.98, m. 46.4°, sapon. no. 82.1, I no. 1.76. Wax from *Doryalis coffra* had  $d_{15}$  1.10, m. 45.5°, sapon. no. 93.6, I no. 1.9.

E. SCHERUBEL

**Residues from the treatment of rice and rice oil.** A. STIELTJES. *Bull. nat. grasses inst. colonial Marseille* **1922**, 201-6.—Rice bran contains  $H_2O$  9.8-11, nitrogenous matter 11.5-15, fat 12.7-15.4, amylaceous matter 40-50, cellulose 5-12 and ash 8-10%. The oil is removed by pressing, 8 to 9% remaining in the cake. Extn. gives better results. An extd. oil had the following const.: sp. gr. 0.918, free fatty acids 7.0%, sapon. no. 179.4, Hehner no. 94.3, glycerol 9.03%, unsapon. 0.7%.

E. SCHERUBEL

**The sulfuric acid reaction for liver oil.** H. D. RICHMOND AND E. H. ENGLAND. *Analyst* **47**, 431 (1922).—Const. results were obtained in testing cod-liver oil by the diln. method (Drummond and Watson, *C. A.* **16**, 3550) by adding 1 cc. of the cod-liver oil to 10 cc. of liquid paraffin (Brit. Pharm.), mixing, and transferring 10 drops of the mixt. to a white porcelain basin, adding 1 drop of  $H_2SO_4$  (Brit. Pharm.) and stirring with a glass rod. If a transient purple color developed, liquid paraffin was added in successive quantities of 5 cc. until no purple coloration was given, and the diln. at which a faint transient purple was seen was recorded. If no purple was seen, successive addns. of 1 cc., 1 cc., 2 cc., and 5 cc. of codliver oil were made.

J. C. S.

**Properties and uses of castor oil.** DOLUIS. *Rev. chim. ind.* **31**, 149-52, 177-80 (1922).—A description of its properties, prepn., and uses.

A. P.-C

**Corn oil as example of conservation by the chemist.** A. F. SIEVERS. *Chem. Age (N. Y.)* **31**, 33-4 (1923).

E. J. C.

**Examination of commercial American soy bean oil.** H. A. GARDNER. *Paint Mfrs. Assoc. of U. S., Circ.* **165**, 117-8 (Jan. 1923).—A list of Am. mills crushing soy beans is given, and analytical results on 2 samples of oil are tabulated. The 1 nos. of these, 119 and 121, are below the values given by imported oils, but in clarity and acidity they are superior.

F. A. WERTZ

**Menhaden oil: from ocean to user.** P. T. BRUYERE. *Oil, Paint & Drug Rep.* **102**, No. 18, 21, 45 (1922).—A brief review of the methods of obtaining fish oil, refining processes, and uses.

F. A. WERTZ

**Pilchard oil.** H. M. LANGTON. *J. Soc. Chem. Ind.* **42**, 47-8T (1923).—The pilchard, *Clupea pilchardus*, is a member of the herring family. The const. of the oil are: sapon. no. 187.8, R.-M. no. 0.50, insol. fatty acids + unsapon. 93.3%, unsapon. 0.98%,  $d_{15.5}$  0.9321, I no. 171.4,  $n_{D20}$  1.47510, viscosity (Redwood) 118. The const. of the mixed fatty acids are: neutralization no. 190.5, mean mol. wt. 291.0, I no. 179.1, m. p. 34.8°, titer 28.2°, ether insol. bromides 56%. Clupanodonic acid is present to the extent of 16.87%. The oil is used in the *manuf. of soft soap*.

E. SCHERUBEL

**Vegetable oil industry.** ED. W. ALBRECHT. *Chem.-Ztg.* **46**, 1034-5 (1922).—Discussion of pressing vs. extn. in the oil industry.

E. SCHERUBEL

**Catalytic hydrogen cleavage.** W. NORMANN. *Chem. Umschau Fette, Oele, Wachse u. Harze* **30**, 3-5 (1923).—U. S. pat. 1,374,589 (C. A. **15**, 2742) is the first publication

on the phenomenon of splitting off  $H_2$  from oils in the presence of catalysts and  $H_2$  gas at temps. above  $220^\circ$ . N. has observed the same phenomenon and cites instances in which the I no. rose during hydrogenation of cottonseed oil from 1 to 6 points after it had dropped to an I no. of 61 in one case and 48 in another. He could not duplicate this action at will, but notwithstanding considers the splitting off of  $H_2$  from oils a demonstrated fact. The U. S. pat. referred to has for its object the production of a better drying perilla oil by first hydrogenating it to an I no. of 90 and then heating it to  $220-50^\circ$ , preferably in an atm. of  $CO$ ,  $N_2$  or  $CO_2$ , until the I no. rises again to 140, resulting in a marked improvement in the drying quality of the oil.

P. ESCHER

**Investigation of perilla oil.** K. H. BAUER. *Chem. Umschau Fette, Oele, Wachse u. Harze* 30, 9-11 (1923).—The unsatd. acids of perilla oil were sepd. by the Pb salt-benzene method and were then brominated in ether and glacial  $AcOH$ . The hexabromides recrystd. from xylene, m.  $181-2^\circ$ . They were debrominated by Zn in alc., boiled with alc.  $KOH$ , acidified, and the acids freed by  $HCl$ , taken up in ether, evapd., dried with  $Na_2SO_4$  and finally oxidized, well cooled, with 1.5%  $KMnO_4$ . The oxidation products were extd. by the Heiduschka-Lüft method successively with gasoline, ether and  $H_2O$ . The gasoline ext. yielded palmitic acid, m.  $59.5-60^\circ$ ; the ether ext. gave dihydroxystearic acid, m.  $131^\circ$ , showing the presence of 5.7% oleic acid, this being contrary to former findings. The  $H_2O$  ext. yielded a mixt. of tetra- and hexahydroxystearic acids. In the filtrate from the oxidation products were found linusinic acid, m.  $203^\circ$ , and isolinusinic acid, m.  $173^\circ$ . Bromination seps. the total amt. of the original linolenic acid as hexabromostearic acid. When this is debrominated and the linolenic acid obtained is again so brominated it yields only 14% as hexabromostearic acid. On oxidation by Hazura's method the regenerated linolenic acid forms isomeric hexahydroxystearic acids in addn. to linusinic and isolinusinic acids. The Hazura oxidation method is not an ideal process for quant. work.

P. ESCHER

**Investigations of perilla oil.** I. K. H. BAUER and R. HARDEGG. *Chem. Umschau Fette, Oele, Wachse u. Harze* 29, 301-5 (1922).—Consts. were:  $d_{20} 0.9280$ ,  $n_D^{20} 1.4830$ , sapon. no. 187.4, I no. (Hanus) 204.4, mean hexabromide no. (Eibner) 50.8%, m. p. of hexabromides  $180^\circ$ . Sepn. into satd. and unsatd. acids by the Pb salt ether method gave 12% satd. and 88% unsatd. acids. The satd. acids were fractionated by Heintz's  $Mg$  pptn. method, yielding 2 final fractions m.  $60-61^\circ$  (palmitic acid) and  $55.5-56.5^\circ$  (probably a mixt. of palmitic with an acid of a higher m. p.). The unsatd. acids were examd. by Hazura's oxidation method with  $KMnO_4$ . Two final  $H_2O$ -sol. products had a m. p. of  $173-175^\circ$  and  $201^\circ$ , corresponding to isolinusinic and linusinic acid (about 25%). The acids difficultly sol. in  $H_2O$  were extd. with petr. ether, ether, alc., and  $H_2O$ , following Heiduschka-Lüft's method (*Arch. Pharm.* 257, 39). The petr. ether ext. furnished insufficient material for examn.; the ether and alc. exts. yielded products that had a m. p. of  $135-140^\circ$ , whose ultimate analyses agreed with tetrahydroxystearic acid. The  $H_2O$  ext. (very large amts. of  $H_2O$  being used) yielded fractions whose m. p. and ultimate analyses indicated mixts. of tetra- and hexahydroxystearic acids (about 26%). When converting these polyhydroxystearic acids into Me esters only  $1/3$  dissolved readily in acetic ester,  $2/3$  remaining insol.; the latter were identified by m. p. ( $155-160^\circ$ ), ultimate analysis, and by the m. p. of the isolated acid ( $160-165^\circ$ ) as a hexahydroxystearic acid mixt. The  $1/3$  portion (sol. in acetic ester) yielded an acid of m. p.  $165^\circ$ , whose ultimate analysis corresponded to (probably a new) hexahydroxystearic acid. **Conclusions:** (1) No dihydroxystearic acid could be obtained; this excluded the presence of oleic acid glycerides. (2) Tetrahydroxystearic acid of m. p.  $135-140^\circ$  was obtained and is probably identical with the  $\gamma$ -tetrahydroxystearic acid of Nicolet and Cox.

P. ESCHER

**Alkalinity determination of lyes.** F. GOLDSCHMIDT. *Z. deut. Oel-Fett-Ind.* 43,

36(1923).—To overcome the difficulty of titrating dark colored lyes with Me orange, G. acidifies 50 cc. of the lye in a 200 cc. flask with 50 cc. of 0.5 N HCl, shakes the soln. with a small quantity of bleaching carbon, fills to the mark and titrates back 100 cc. of the soln. The filtrate may be used for glycerol detn. by using  $\text{H}_2\text{SO}_4$  in place of HCl for the titration.

P. ESCHER

**Washing soaps and their valuation.** MAURICE DE KEGHEL. *Rev. chim. ind.* 30, 332-41(1921).—A general discussion. A. P.-C.

**Solvent soaps.** A. CHAPLET. *Rev. chim. ind.* 31, 206-13(1922).—Description of the prepn. and uses of benzene, petroleum, and sulfonated oil soaps. A. P.-C.

Mutual solubility of hydrocarbons, fatty oils and liquid sulfur dioxide (ZERNER, *et al.*) 22. Oil refining (Can. pat. 227,885) 22.

**Purification of crude castor oil.** YOSHIBUMI KUME. Japan. 40,191, Oct. 4, 1921. A mixt. of crude castor oil and 25% astringent juice prepd. from persimmons is heated in a closed vessel at  $100^\circ$  for 40-50 min. under agitation and sepd. from the ppt. It is then mixed with the same quantity of glacial AcOH and sprayed into a chamber satd. with superheated steam and having a filter in the bottom. The filtrate is neutralized with  $\text{Ca}(\text{OH})_2$  soln., sepd. from the aq. layer, mixed with 6-8% Japanese acid clay, heated to  $70-80^\circ$  and filtered. The oil is mixed with twice its vol. of  $\text{H}_2\text{O}$  contg. 2-5% of a mixt. of  $\text{Na}_2\text{CO}_3$  and  $\text{NH}_4\text{OH}$ , heated to  $100^\circ$ , sepd. from the  $\text{H}_2\text{O}$  layer, washed with warm  $\text{H}_2\text{O}$ , heated to  $70-80^\circ$  with 10% Japanese acid clay, filtered, and hot air is blown through it for 3-5 hrs. The product is suitable for lubricant for high-speed machines.

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Armand Vivien. ANON. *Rev. agr. Maurice* 1, 306-7(1922).—An obituary.

F. W. ZERBAN

**Sugar deterioration; its cause and some suggested remedies.** W. M. McQUAID. *Sugar Central and Planters News* 3, 592-4(1922).—Rapidity of working and scrupulous cleanliness at all stations are emphasized. Well dried 96 test sugar of uniform, medium-size grain well coated with molasses keeps best. Washing with water and any opportunity for the bagged sugar to pick up moisture during transport or storage must be avoided.

F. W. ZERBAN

**Progress in the beet-sugar industry in 1922.** E. O. VON LIPPMANN. *Chem.-Ztg.* 47, 89-91(1923).

E. H.

**Simultaneous saturation applied to beet juices treated with magnesium bicarbonate.** K. ANDRLIK and W. KOHN. *Z. Zuckerind. Czechoslovak. Rep.* 46, 404-10, 411-5 (1922).—Beet juices, sirups, and molasses were treated in the lab. with sufficient lime to impart an alk. of about 0.1%, filtered, mixed with a soln. of Mg bicarbonate, and submitted to the process of simultaneous satn. previously described (Urban, C. A. 16, 3553). A considerable diminution of the color and an appreciable increase in the purity of the product thus clarified resulted. Mg bicarbonate was prepd. for this purpose from dolomitic lime by dissolving out the  $\text{Ca}(\text{OH})_2$  with a soln. of sucrose and carbonating the residue.

J. S. C. I.

**Determination of reducing sugars.** T. BONWETSCH. *Centr. Zuckerind.* 30, 495-6(1922).—After the reduction of the Fehling soln. following the Herzfeld or other

method, the  $\text{Cu}_2\text{O}$  is dissolved from the filter paper, and converted into cuprammonium sulfate, the amt. of the latter compd. being detd. colorimetrically. J. S. C. I.

**Estimation of caramel in sugar products. Criticism of the Ehrlich method.** G. P. MEADE. *Ind. Eng. Chem.* 15, 275(1923).—While it is true that Ehrlich's saccharan (C. A. 3, 2881) is not pptd. by basic  $\text{Pb}(\text{AcO})_2$  when in soln. by itself, it is, like any other caramel prepn., carried down partly or completely by the ppt. obtained when either neutral or basic  $\text{Pb}(\text{AcO})_2$  is added to sugar products. Caramel can therefore not be detd. in sugar products by adding basic  $\text{Pb}(\text{AcO})_2$  soln. and comparing the color of the filtrate with that of a standard saccharan soln. F. W. ZERBAN

**Defecation experiments with cane sugar juice.** D. J. W. KREULEN. *Chem. Weekblad* 19, 409-11(1922).—(1) Cane juice (250 cc.) was boiled with 21.5 g. lime. (2) The same amt. of the juice was heated to  $85^\circ$  and the same quantity of lime added. (3) The juice was first boiled and the lime added, afterwards. In (3) the quantity of ppt. was largest and the clearest juice was obtained. R. BEUTNER

**Sumacel.** P. DE SORNAY. *Rev. agr. Maurice* 1, 323(1922).—This is a diatomaceous earth contg. 80%  $\text{SiO}_2$ , 5.3%  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , 2.02%  $\text{CaO}$ , 8.16%  $\text{H}_2\text{O}$ , 2.12% volatile matter, and traces of  $\text{MgO}$ . It is suitable for a filtration aid in sugar manuf. F. W. ZERBAN

**Sumaphos.** P. DE SORNAY. *Rev. agr. Maurice* 1, 324(1922).—This is a mixt. of diatomaceous earth and acid phosphate, contg. 16.68% of the former, 36.22%  $\text{P}_2\text{O}_5$  sol. in water, and 0.7%  $\text{P}_2\text{O}_5$  insol. in water. It is recommended for use in the manuf. of white sugar. F. W. Z.

## 29—LEATHER AND GLUE

ALLEN ROGERS

**Report of the Commission of the French Section of the Society of Leather Trades' Chemists on the quantitative analysis of tanning materials.** G. HUGONIN. *J. Soc. Leather Trades Chem.* 7, 6-36(1923).—Sec C. A. 17, 349. E. J. C.

**The manufacture of artificial leather.** MAURICE DE KEGHEL. *Rev. chim. ind.* 30, 7-10, 35-40(1921).—An outline of a large number of processes used and proposed. A. P. C.

**Supplement to the "chroming of formaldehyde leather."** E. GRILICHES. *Collegium* 1922, 286-7; cf. C. A. 17, 351.—Varying amts. of acid or alkali exert an influence on the chrome absorption.  $\text{CH}_2\text{O}$  alone does not essentially alter the absorption of chrome by leather. C. T. WHITE

**The determination of free sulfuric acid in leather.** C. VAN DER HOEVEN. *Collegium* 1922, 282-5; cf. C. A. 16, 850.—Ten g. finely prepd. leather is extd. at  $55^\circ$  for 2 hr. with an 8% soln. of  $\text{NaH}_2\text{PO}_4$  until the ext. amts. to 500 cc. The sample is then washed with distd.  $\text{H}_2\text{O}$  at  $55^\circ$ ; the wash  $\text{H}_2\text{O}$  is then added to the ext. previously obtained. In this soln. the  $\text{SO}_4$  is detd. in the usual manner as  $\text{BaSO}_4$ . Insol.  $\text{SO}_4$  in the leather is detd. by analysis of the ash. The difference between the total  $\text{SO}_4$  found and that inorganically combined, which is detd. in the ash of a sep. sample, is calcd. as  $\text{H}_2\text{SO}_4$ . This wt. is reported as the free  $\text{H}_2\text{SO}_4$  in the leather. C. T. WHITE

**Pancreatin as an unhairing agent.** J. A. WILSON AND A. F. GALLUN, JR. *Ind. Eng. Chem.* 15, 267-9(1923).—When calf skin is swollen in dil.  $\text{NaOH}$ , neutralized with  $\text{NaHCO}_3$ , and then put into pancreatin soln. at  $25^\circ$  exposed to air, the hair is loosened, but the action is not due to the enzyme, since it is checked by covering the soln. with toluene. Neither is any elastin removed from the skin by the enzyme at  $25^\circ$ . At  $40^\circ$ , even under toluene, the enzyme causes a complete sepn. of hair and epidermis from



the skin and simultaneously hydrolyzes the elastin fibers, effecting both unhairing and bating in a single bath. Previous soaking in NaOH soln. is necessary in order to render the corneous layer of the epidermis permeable to the enzyme. J. A. W.

**The black wattle industry.** T. R. SIM. *S. African J. Ind.* 5, 467-72, 519-25 (1922); 6, 27-35 (1923). E. J. C.

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**Chinese tannin (HERZIG) 10.** Water-soluble derivatives of aryl ethers of higher aliphatic alcohols (Ger. 344,878) 10.

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**Leather-like material from intestines.** E. MARKUS. U. S. 1,444,548, Feb. 6. Sol. salts and "glutens" are removed from intestines by washing and the cells of the fibrous tissue are then filled with insol. ppts. such as are formed from  $\text{NH}_4$  oxalate,  $\text{CaCl}_2$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{BaCl}_2$  which are fixed by the use of  $\text{FeCl}_3$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$  or other compds. adapted to unite with the substance of the cells. Products thus prepd. are similar to leather.

**Leather packings.** M. H. COOK. U. S. 1,443,311, Jan. 23. Oils are extd. from rawhide by solvents; packing cups or similar articles are formed by cementing the treated rawhide to oak-tanned leather; the rawhide is then treated to restore the oils and fats extd. from it and the leather is impregnated with shellac or paraffin to stiffen it.

**Tanning.** E. SCHWARZ and L. BLANGEY. Can. 228,243, Jan. 23, 1923. Hides are treated with a bath contg. sulfonated crude carbazole.

**Tanning material.** O. SCHMIDT. Can. 228,241, Jan. 23, 1923. A tanning material from naphthalene,  $\text{H}_2\text{SO}_4$  and  $\text{HCHO}$  is amorphous, sol. in water, free from phenolic hydroxyl and quinone groups and dyeing properties; it will ppt. glue or gelatin.

**Tanning composition.** C. IMMERHEISER and HUGO WOLFF. Can. 228,246, Jan. 23, 1923. A dil. acid soln. of sulfonated crude anthracene gives a pure brown color to hide suspended therein. The compd. may be treated with  $\text{Cl}$  and may contain oxalic acid.

**Tanning composition.** R. B. CROAD. U. S. 1,443,697, Jan. 30. At least 2 mols. of mixed cresols or a similar aromatic hydroxy compd. and 1 mol. of  $\text{CH}_2\text{O}$  are condensed in the presence of an alk. condensing agent such as  $\text{NH}_4\text{OH}$  and the product is sulfonated with at least 1 mol. of  $\text{H}_2\text{SO}_4$  or other sulfonating agents. The sulfonated product is condensed with at least a half mol. proportion of  $\text{CH}_2\text{O}$  or similar aldehyde and partially neutralized, e. g., with  $\text{ZnO}$  or  $\text{Ca}(\text{OH})_2$ .

**Tanning agents.** C. IMMERHEISER and F. HASSLER. Can. 228,245, Jan. 23, 1923. Tan wood is treated with a soln. of an aromatic sulfonic acid which is capable of pptg. glue from acid solns.

**Soluble tanning agent.** O. SCHMIDT. Can. 228,242, Jan. 23, 1923. A difficultly sol. tanning agent is made more sol. by treating it with a product obtained from naphthalene 10,  $\text{H}_2\text{SO}_4$  10, and  $\text{HCHO}$  4.3 parts.

**Soluble tanning agent.** F. HASSLER. Can. 228,244, Jan. 23, 1923. A readily sol. tanning compn. contains a natural tan and a sulfonic acid (or its salt) of an at least tricyclic hydrocarbon.

**Soluble condensation products of naphthalene, formaldehyde and sulfuric acid.** O. SCHMIDT. Can. 227,609, Jan. 2, 1923. Naphthalene and  $\text{H}_2\text{SO}_4$  are heated at about  $140^\circ$  to form  $\beta\text{-C}_{10}\text{H}_7\text{SO}_3\text{H}$  and when the product is cooled to  $80\text{-}90^\circ$   $\text{CH}_2\text{O}$  is gradually added while the temp. is kept at  $60\text{-}100^\circ$ . The mass thickens and water is added to facilitate stirring which is continued until  $\text{CH}_2\text{O}$  odor is eliminated. On cooling the material solidifies to a resinous slightly colored mass easily sol. in cold  $\text{H}_2\text{O}$ . When the soln. is neutralized with an alkali the products are still sol. The soln. is suitable for

use in rendering sol. the difficultly sol. portion of quebracho ext. used in tanning. It may be used as a *tanning agent* itself.

### 30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

**Progress in rubber research during 1922.** I. H. W. GREIDER. *India Rubber Rev.* 22, No. 12, 9-11(1922).—Chem. advance, with numerous references.

C. C. DAVIS

**Rubber.** H. P. STEVENS. *Brit. Assoc. Advancement Sci., 4th Rept. 1922*, 357-80.—A discussion of the properties of rubber from the colloidal point of view including: raw rubber sols and gels (including mastication, "crèping" coagulation of latex, influence of protein constituents, etc.); effect of vulcanization on dispersion; changes in phys. properties consequent upon vulcanization; chem. changes due to vulcanization; correlation of phys. properties and chem. compn. (coeff. of vulcanization); effect of catalysts on phys. properties; reversion of the stress-strain curve; variation in proportion of S to rubber; effect of mineral ingredients; alternative methods of vulcanization; theories of vulcanization; other reactions of the caoutchouc hydrocarbon; synthetic rubber. An extensive classified bibliography is appended, bringing up to date that of the First Report.

JEROME ALEXANDER

**Rubber prepared by spraying latex.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 41-8(1923).—The difference between the wt. of the product obtained from latex by coagulating it and converting the coagulum into crêpe and the wt. of total solids in the latex is not const., but varied in 10 samples from 5.8 to 14.1% of the wt., of the latter, the mean difference being 9.3%. Hence, as air-dried rubber prep'd. by the spray desiccation of latex (cf. C. A. 16, 3332) was found to contain 2-3% of moisture, the yield of such rubber may be greater than the yield of crêpe prep'd. by the usual procedure by ams. ranging from 8 to 17%. A sample of sprayed rubber showed an acetone ext. of 4.8%. The ext. was hygroscopic. Wet crèping affected the rubber only slightly, and even prolonged soaking in water failed to remove the whole of the water-sol. material in the rubber. Sprayed rubber and ordinary crêpe prep'd. from the same sample of  $\text{NH}_4$ -preserved latex were compared in vulcanization tests made at 138° in the mixt. rubber 90:S 10. The sprayed rubber showed a higher rate of cure (times of cure: 108 and 137 mins., resp.), but a lower breaking stress (13.4 as compared with 14.1 kg./cm.<sup>2</sup>) than the crêpe rubber. The higher rate of cure of the sprayed rubber is attributed to the retention of sol. serum constituents; its lower tensile strength to the presence of inert serum substances. S. subjects the spray method of prep'g. rubber to a crit. review.

G. S. WHITBY

**Estimation of dry rubber in latex.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 59-60(1923).—For evaluating latex a mere detn. of the total solids obtained on evap. the latex is not suitable, as the first sentence of the preceding abstr. will indicate; and it is concluded that the only satisfactory method is to coagulate the latex with  $\text{H}_2\text{SO}_4$  (following it up by alc. in cases where  $\text{H}_2\text{SO}_4$  alone does not give complete coagulation), to convert the coagulum into thin crêpe, and to dry the product at 70°. G. S. W.

**Carbon black in compounding.** E. L. DAVIES. *India Rubber Review* 22, No. 12, 16; 19; 134(1922).—A general description of the properties, uses and effects of C black in rubber compds. It is suggested that in virtue of its adsorption capacity C black be used as a medium for introducing curatives, gases, etc., into rubber. C. C. D.

**Thermal properties of various pigments and of rubber.** IRA WILLIAMS. *Ind. Eng. Chem.* 15, 154-7(1923); cf. C. A. 15, 2749.—The *thermal cond. and diffusivity of rubber and of pigments* are det'd. by 2 new methods. Method (1) consists in passing

steam through a closed cylindrical cell covered with the material and measuring the  $H_2O$  condensed. The outside temp. is controlled by a const.-temp. bath. Method (2), adapted from that of Williamson and Adams (cf. *C. A.* **14**, 3185), gives the diffusivity const. from which the cond. is calcd. by the following relation: diffusivity = cond./ $(\text{sp. heat} \times d.)$ . (1) is the more accurate, but (2) is much more rapid and is accurate enough for most work. The following data give the cond. in cal. per cc. per sec. at 45–100°: ZnO 0.00166, S 0.00012, whiting 0.00084, PbO 0.00051, lithopone 0.00094, talc 0.00058, Sb sulfide contg. 15.6% S 0.00021, red oxide 0.00132, gas black 0.00067, blanc fixe 0.00078, Dixie clay 0.00058,  $MgCO_3$  0.00103, smoked sheets, pale crêpe, etc., cured and uncured 0.00032, cord fabric 0.00082. Since cond. is an additive property depending upon the vol. %, the cond. const. is the sum of the vol. %  $\times$  cond. of the individual ingredients.

C. C. DAVIS

**The direct determination of rubber hydrocarbon as bromide.** M. PONTIO. *Chimie et industrie* **8**, 1211–2(1922).—P. briefly criticizes Buddes' method, and describes his modification of it. Treat 2 g. of sample with 200 cc. of xylene in a water bath (soln. is usually complete in 1 hr.), cool to 15°, make up to 200 cc., let stand till all insol. matter has settled out; to a 20-cc. aliquot add 50 cc. of a soln. of 3 cc. of  $Br_2$  in 247 cc. of  $CHCl_3$  or of  $CCl_4$ , let stand 15 min., add 250 cc. of  $Me_2CO$ , stir, and filter immediately through balanced filter papers, receiving the material on one filter and passing the filtrate through the second one. Wash thoroughly with  $Me_2CO$  and then with abs. alc., dry to const. wt. at 70–80° (about 2 hrs.), weigh, ignite, and subtract the wt. of ash from the wt. of the ppt. The bromide obtained is very white and stable, and, after drying, is insol. in petr. ether, benzine,  $CHCl_3$ , kerosene, pyridine, aniline, spirits of turpentine,  $CCl_4$ ,  $Me_2CO$ , and amyl acetate. It is attacked readily by fuming  $HNO_3$  and by  $H_2SO_4$ , with difficulty by 36° Bé.  $HNO_3$ , and not at all by  $HCl$ . On heating to 110° it does not change in wt. but is slightly discolored. Carius', Chablay's and calcination with  $CaO$  methods gave 60.1, 68.3, 68.3% Br, resp. Factor 0.317 corresponds to  $(C_{10}H_{16})_2Br_{11}$  (C 27.96, H 3.75, Br 68.28%). The results obtained by this method and by difference on a no. of deresinified and of crude rubbers are given, showing complete concordance in the first case (except 1 sample), while the Br method gives slightly higher results in the second case, probably owing to the presence of the resins.

A. P.-C.

**Water dispersions from coagulated rubber, balata, and gutta-percha.** J. B. TUTTLE. *India Rubber World* **67**, 291–3(1923); cf. *C. A.* **17**, 900.—Preliminary expts. show that dispersions contg. not only rubber but also an accelerator, such as aniline, and a compounding ingredient, such as ZnO, can be made successfully, and, when coagulated, yield a vulcanizable product. Rubber applied from an artificial water dispersion to fabric treated with a sulfur-terpene product (*C. A.* **16**, 856) is vulcanizable. It is believed that artificial water rubber dispersions have advantages over latex for the impregnation of fabric and of paper pulp.

G. S. WHITBY

**The acceleration of vulcanization by cinchona alkaloids.** B. J. EATON AND R. O. BISHOP. *J. Soc. Chem. Ind.* **41**, 374–6T(1922).—Quinine, cinchonine, and cinchonidine have practically identical accelerating power. Less active than these are quinidine and the similar or identical "Accelerator X." These substances all show greater, but not very much greater, activity in the presence than in the absence of ZnO. They all affect the rate of vulcanization of crêpe to a greater extent, both relatively and absolutely, than that of slab, but do not, even in the presence of ZnO, overcome the differences found in unaccelerated pure gum mixts., both in regard to rate of cure and maximal tensile strength, between these 2 forms of rubber. The standard curve used by E. for deciding the optimum cure in 90:10 rubber-S mixts. cannot be applied when 4 parts ZnO has been added to the mixt., as the introduction of ZnO alters the type of the curve. The following figures indicate broadly the degree of potency of the accel-

erators mentioned. One part reduces the time of cure of a 90:10:4 rubber-S-ZnO mixt. from 60 to 30–15 min. in the case of slab rubber; and from 135 to 45–25 min. in the case of crêpe rubber.

G. S. WHITEY

**The aging of rubber.** S. A. BRAZIER. *India-Rubber J.* 65, 183–9(1923).—A review.

G. S. WHITEY

Rubber latex in the paint industry (GARDNER, YARNALL) 26. Future supply of carbon black (CARR) 18.

**Rubber.** W. FROST and H. FROST & Co., LTD. Brit. 186,709, July 5, 1921. A compn. for the repair or jointing of rubber articles consists of a rubber compn. capable of being vulcanized by heat, to which has been added sufficient amt. of a solvent (30–40%), such as  $\text{CCl}_4$  or naphtha or a mixt. of these, to produce an adhesive capable of being extruded from a collapsible tube, but which will retain any shape to which it is molded.

**Rubber composition.** W. E. GARDNER. U. S. 1,440,455, Jan. 2. A vulcanizable compn. adapted for the manuf. of molded insulators is formed of rubber 25 parts or less, siliceous earth 60 or more, glue-sized mica 5,  $\text{Ca}(\text{OH})_2$  2 and S 8 parts.

**Rubber composition.** P. SCHIDROWITZ. U. S. 1,443,149, Jan. 23. A compn. adapted for vulcanization without coagulation is formed by treating rubber latex with a small amt. of  $\text{NH}_3$  to render it alk. and then mixing it with S, ZnO and vulcanization accelerators.

**Rubber sheets.** G. B. BRITTON. U. S. 1,440,371, Jan. 2. Rubber is treated with  $\text{H}_2\text{O}$  while it is being formed into sheets, in order to cleanse it, and the sheets are dried by passing them over heated rolls.

**Dipped rubber goods.** M. M. HARRISON. U. S. 1,445,080, Feb. 13. Butyraldehyde 3–10% is added to rubber cement to form a soln. adapted for the manuf. of dipped rubber goods such as finger cots or surgeon's gloves.

**Oils from rubber waste.** C. LEBEVRE. Brit. 188,008, May 9, 1921. An oil, having the properties of oil of turpentine, is obtained by heating rubber waste to about  $220^\circ$ , condensing the vapors given off, and rectifying this liquid by distn., preferably with steam.

**Puncture-sealing composition.** Soc. J. HOUDRY ET FILS. Brit. 187,594, Oct. 9, 1922. A compn. for automatically sealing punctures in tires consists of a mixt. of a substance having a base of cellulose, a basic soln. and a weak acid, to which may be added asbestos, kieselguhr, antiseptic and coloring matters. Suitable ingredients and proportions are: bran 30,  $\text{Na}_2\text{CO}_3$  2.1, salicylic acid 5.4, asbestos 36, kieselguhr 4 kg., sapocresol 2.5 l., turpentine 500 cc., creosote 150 g., Soudan red 50 g., alc. 40 l., and sufficient  $\text{H}_2\text{O}$  to make up 600 l. The bran is boiled with some of the  $\text{H}_2\text{O}$ , and the soda soln. is added. After cooling the acid is added, and subsequently the other ingredients with const. kneading until a homogeneous product results. Dil. HCl may replace the salicylic acid.

**Protection of bale of unvulcanized rubber.** E. HOPKINSON. U. S. 1,442,218, Jan. 16. The surface of a bale of unvulcanized rubber is protected against oxidation or other damage by a thin layer of brominated product formed by treating the surface with a 3% soln. of Br in  $\text{CCl}_4$ . Cl, I and S chloride also may be similarly used.

**Preserving uncured rubber.** H. J. BUTLER. U. S. 1,444,061, Feb. 6. A sheet of uncured rubber is mounted on a sheet of parchment paper so that it is convenient for handling.

**Vulcanizing rubber.** E. RICARD. U. S. 1,440,176, Dec. 26. Furfuramide, oxyfurfuraniline, furfuromethylaniline, furfurylamine, furfurine, furfuroidianiline, furfuro-

toluidine, furfurodiphenylamine or furfurophenylhydrazine is used as a vulcanization accelerator and "vitalizer" in rubber compns.

**Vulcanizing rubber.** I. OSTROMISLENSKY. U. S. 1,433,093, Oct. 24. Rubber ozonide or a similar rubber compd. contg. O is added to rubber compns. to serve as a vulcanizing agent.

**Vulcanizing rubber.** C. E. BRADLEY and S. M. CADWELL. U. S. 1,444,865, Feb. 13. Rubber compns. are mixed with triethyltrimethylenetriamine or other formaldehyde condensation product of aliphatic amine in order to accelerate vulcanization with S.

**Accelerating rubber vulcanization.** S. J. PRACHEY. U. S. 1,443,381, Jan. 30. *p*-Nitrosodimethylaniline and S are heated together at 180-135°, and the reaction residue and condensed vapors formed are utilized as vulcanization accelerators.

**Sealing mixture for pneumatic tires.** H. H. WARMUND. U. S. 1,444,288, Feb. 6. A compn. for sealing punctures in pneumatic tires, rubber tubing or similar articles is formed of sugar, rice, a soln. of rubber, waste sulfite cellulose liquor and talcum. Cf. C. A. 17, 228.





